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The Application of Electrochromic Character of PANI Film in Hydrogen Phosphate Ion Detection

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Excessive emissions of anions severely damaged the ecological balance of water environment. Therefore, anionic online detection played an important role in our lives. Compared to chromatographic technique and colorimetric sensors and fluorescence sensors, Electrochemistry detect anion presents several advantages such as operation simple, high sensitivity, fast response, improved selectivity, miniaturization and online detection. This work fabricated the PANI/ITO electrode by electrochemical polymerize polyaniline film on ITO electrode. We make use of the PANI/ITO electrode detected different concentration hydrogen phosphate ion. The results indicate that with the concentration of hydrogen phosphate ion increased, redox peak potential of the cyclic voltammetry curves of PANI film changed obviously, impedance of PANI film increased with anion concentration. The limits of detection of hydrogen phosphate ion could achieve 0.023 mol/L.

Keywords: PANI/ITO electrode, Hydrogen phosphate ion detection, Electrochromism

1. INTRODUCTION

With the widespread use of chemical fertilizer and pesticide, a large number of anion discharged in the environment. Phosphate ion flows into water by kinds of ways, and make a large area of water eutrophication[1],the plants in water grow quickly and threaten other creatures which live in water, it heavy damage the ecological balance of water environment.

Among the methods of detect and recognize anions, chromatographic technique[2-4] could recognized well, but the complicated operation of equipment and the long detection cycle cannot satisfy the on-line detection. Colorimetric sensors[5-9] and fluorescence sensors[10-12] can also recognize anion effectively, but the carrier used in recognize anion cannot be reused, it will make the secondary pollution to environment.

Electrochemistry methods detect hydrogen phosphate ion have been attracting increasing attention. Make use of electrochromic character[13] of PANI film in hydrogen phosphate ion detection has a lot of advantages. PANI film has been widely used as active layers of Electrochromic devices[14,15] since it can reversibly change colors upon electrochemical doping and de-doping treatments[16,17].

This work developed an electrochemical method polymerize polyaniline film on ITO electrode by potentiostatic. We introduced sulfate ion in the polymerized polyaniline film by sulfuric acid electrolyte. We prepared PANI/ITO electrode in 1.0 mol/L H_2SO_4 solution. This paper make use of the PANI/ITO electrode detected different concentration hydrogen phosphate ion.and get the selectivity of the PANI/ITO electrode for hydrogen phosphate ion by cyclic voltammogram, UV-vis spectrum and impedance spectra.

2. EXPERIMENTAL PART

2.1. Apparatus & Materials

All the electrochemical analyses were performed using a CHI 660C electrochemical workstation (CH Instruments, Austin, TX). The absorbance was measured with a spectrophotometer (Shimadzu UV-2550; Shimadzu, Kyoto, Japan) at 800 nm against a blank. The ITO conductive glass was purchased from ZhuHai Kaiwei electronic components Co., LTD. All reagents were purchased from Sigma-Aldrich Co. and used without further purification.

2.2. Preparation of PANI/ITO Electrode

An ITO electrode (0.5 cm × 2.0 cm) was polished by Al_2O_3 powder. Ultrasonic washed 5 minutes with deionized water, ethanol and acetone, respectively. Then, take it out and dry under nitrogen atmosphere before use. Cyclic voltammetry measurements were carried out at room temperature in a three-electrode cell, with Pt wire as the auxiliary electrode, KCl-saturated Ag/AgCl electrode as the reference electrode, and the ITO electrode as the working electrode, respectively. The fabrication process was carried out in 1 mol/L H_2SO_4 solution of 0.01 mol/L (about 45.5 μL) aniline. Conductive polyaniline film was polymerized on the ITO electrode under 0.8 V by potentiostatic method. The prepared PANI/ITO electrode washed with deionized water, in order to wash away the aniline monomers on the surface of electrode.

2.3. PANI/ITO Electrode for Hydrogen Phosphate Ions Detection

Place the PANI/ITO electrode in a quartz glass tube equipped with 1 mL 1 mol/L H_2SO_4 solution. Add 10 μL 0.01 mol/L Na_2HPO_4 in the solution. Put the tube in the UV spectrograph, and place in the reference electrode and the auxiliary electrode. The cyclic voltammetry between -0.6 V and 1.0 V (vs.Ag/AgCl) at a scan rate of 100 mVs^{-1}. At the same time, UV-vis spectra scan at the wavelength of 800 nm.

2.4. Impedance Measurement of PANI/ITO Electrode

The impedance measurement performed in a three-electrode cell containing 2 mL 1 mol/L H_2SO_4 solution (voltage: 0.3V, HF: 10000 Hz, LF: 0.01 Hz). Add 10 μL 0.01 mol/L Na_2HPO_4 in the solution each time.

3. RESULTS AND DISCUSSIONS

3.1. CV Behavior of PANI/ITO Electrode with Different Concentrations of Na_2HPO_4

As seen in Figure 1, PANI/ITO electrode at different concentration of H_2SO_4 electrolyte solution of Na_2HPO_4, the redox potential gradually shifts to the negative potential direction. Overall, the redox potential moved to high potential direction. At the same time, peak current is also gradually reduced. During CV scanning, SO_4^{2-} in the PANI film was replaced with dissociative HPO_4^{2-} in electrolyte solution.

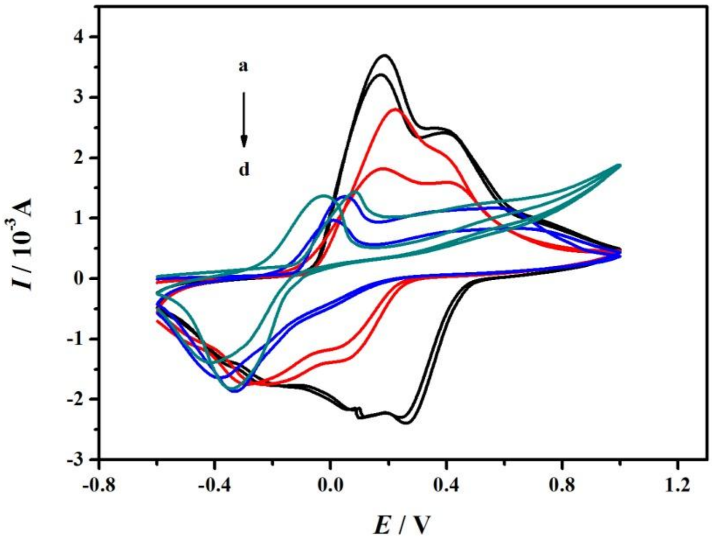


Figure 1. Cyclic voltammograms of PANI/ITO electrode in 2 mL H_2SO_4 contain different concentrations of Na_2HPO_4, scan range: -0.6V~1.0V, scan rate: 100mV/s, n=2 (a-d: 0, 0.25, 0.5, 0.75 mmol/L, respectively)

3.2. Impedance Measurement of PANI/ITO Electrode with Different Concentrations of Na_2HPO_4

Figure 2 is the impedance of PANI/ITO electrode with different concentration of Na_2HPO_4. When the concentration of Na_2HPO_4 increased, the impedance spectrum of semicircle diameter gradually increased. Thus it can be seen electrode surface electron transfer impedance gradually increased. It proved that HPO_4^{2-} instead of SO_4^{2-} ion got into the PANI film successfully.

PANI film has certain size memory ability on polymerization process of doping ions[18,19]. After de-doping, PANI film skeleton still kept SO_4^{2-} ion size space, therefore HPO_4^{2-} ion came into

PANI skeleton, but it cannot completely fill the cavity from SO_4^{2-}. It caused that inside of PANI film still has certain gap, the gap could lead to increase the distance of electron transfer in the membrane, so as to increased internal impedance of the membrane.

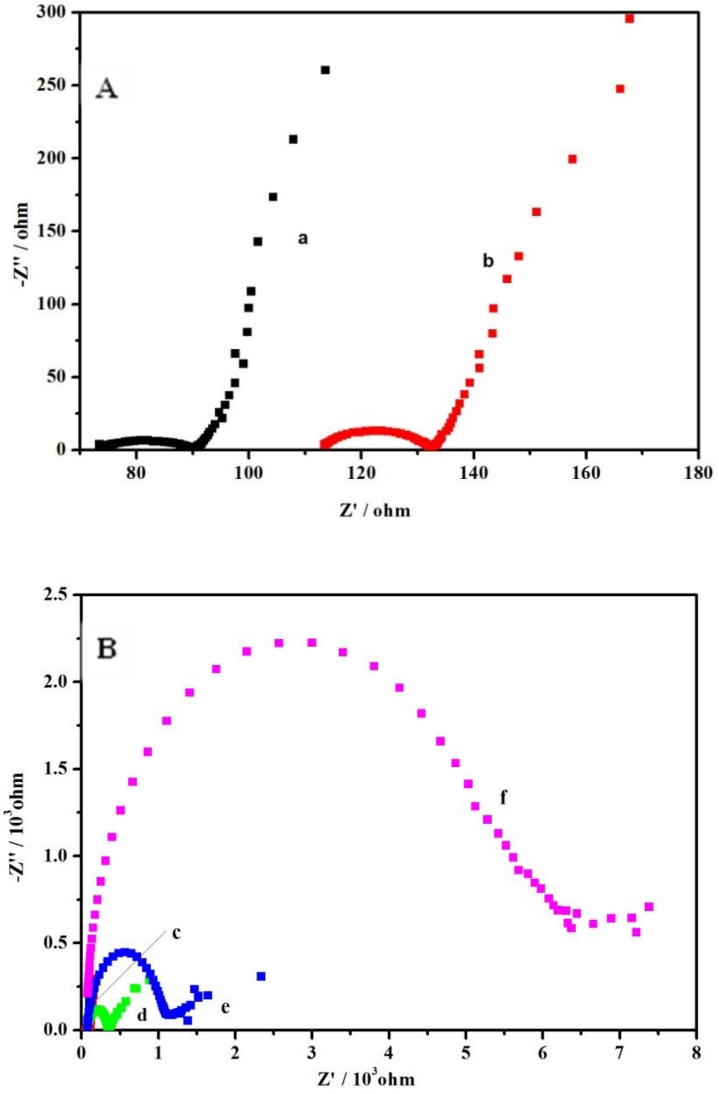


Figure 2. Impedance spectra of PANI/ITO electrode in 1 mol/L H_2SO_4 solution with different concentration Na_2HPO_4. Voltage: 0.4V, high frequency: 10000 Hz, low frequency: 0.01 Hz (a-d: 0.05, 0.1, 0.15, 0.20 mmol/L, respectively)

3.3. Abs Spectra of PANI/ITO Electrode with Different Concentrations of Na_2HPO_4

In Figure 3, UV spectrums appeared the same two ultraviolet absorption peaks in two laps of CV scanning process. Thus, inside the PANI film, it happened reversible electrochromic reaction during the electrochemical redox process. When t=0, the absorbance of PANI film is minimum. This is because the CV scanning of PANI film began from negative potential, the PANI film is reduction state at the moment. But along with CV scanned to positive potential, PANI film gradually proton- ated and changed to oxidation state, and the absorbance of PANI film is increased. With the increase of the concentration of Na_2HPO_4, the value of PANI film ultraviolet absorption peaks gradually reduced. This could be during the protonation of the PANI film and the process of transform to oxidation state. Due to the HPO_4^{2-} concentration increased, more SO_4^{2-} anion in PANI film be replaced, led to the absorbance of doped PANI film gradually reduced. The variation of absorbance of PANI film in the oxidation state could be applied to HPO_4^{2-} ion detection[20].

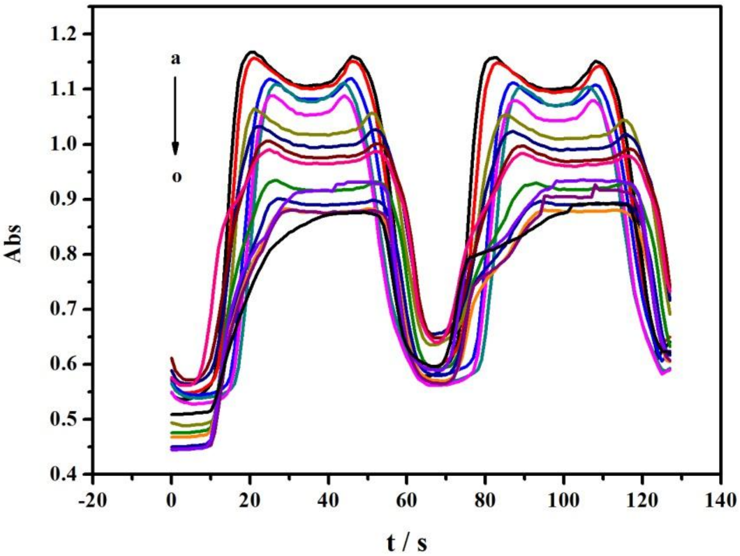
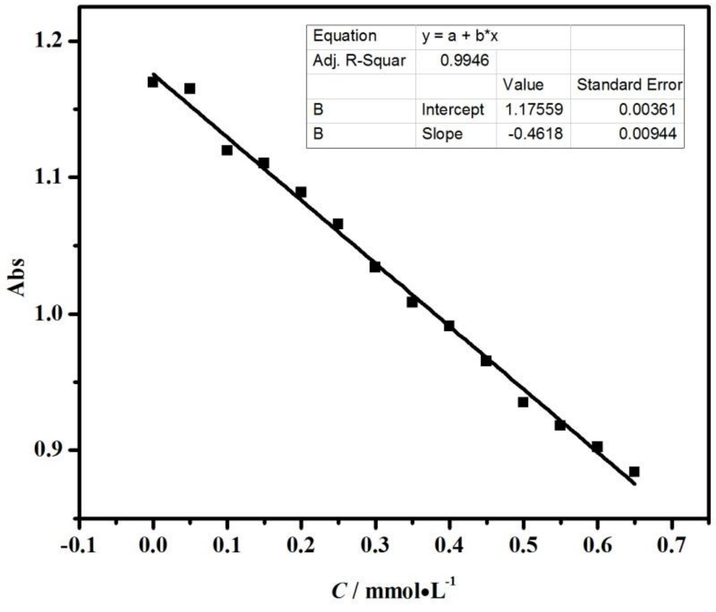


Figure 3. Ultraviolet absorption spectra of PANI/ITO electrode in 1 mol/L H_2SO_4 solution with different concentration Na_2HPO_4 at CV scan, scan rate,100mV/s, n=2, λ=800nm. (a-o:_0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75 mmol/L, respectively)



Equation	y = a + b*x		
Adj. R-Squar	0.9946		
		Value	Standard Error
B	Intercept	1.17559	0.00361
B	Slope	-0.4618	0.00944

Figure 4. Linear relation of absorption peaks of PANI/ITO electrode and concentration of Na_2HPO_4

From the Figure 4 can be seen, with the concentration of HPO_4^{2-} increased, absorption value of the oxidation state of PANI film gradually reduced. From the linear relationship, R^2= 0.9946, and calculated the limits of detection of hydrogen phosphate ion could achieve 0.023 mol/L.

3.4. Stability Test of PANI/ITO Electrode

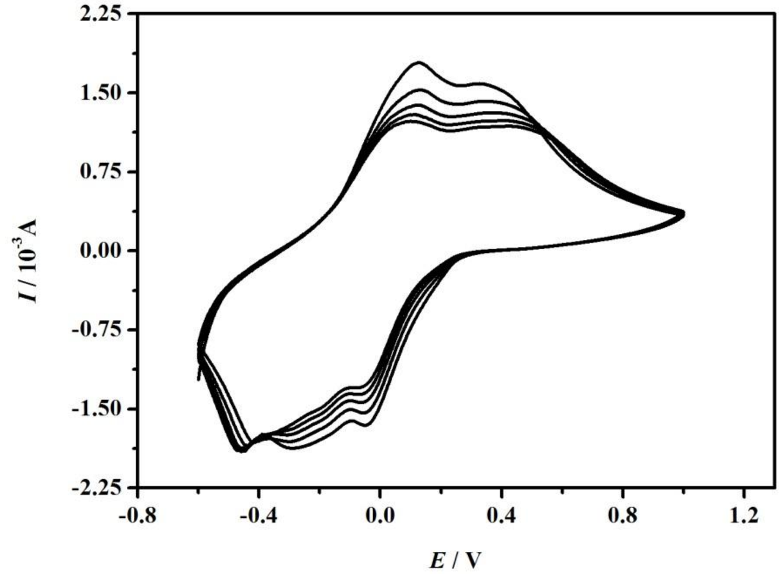


Figure 5. Cyclic voltammograms of PANI/ITO electrode in 2 mL H_2SO_4 cuvette, scan range: -0.6V~1V, scan rate: 30mV/s, n=5.

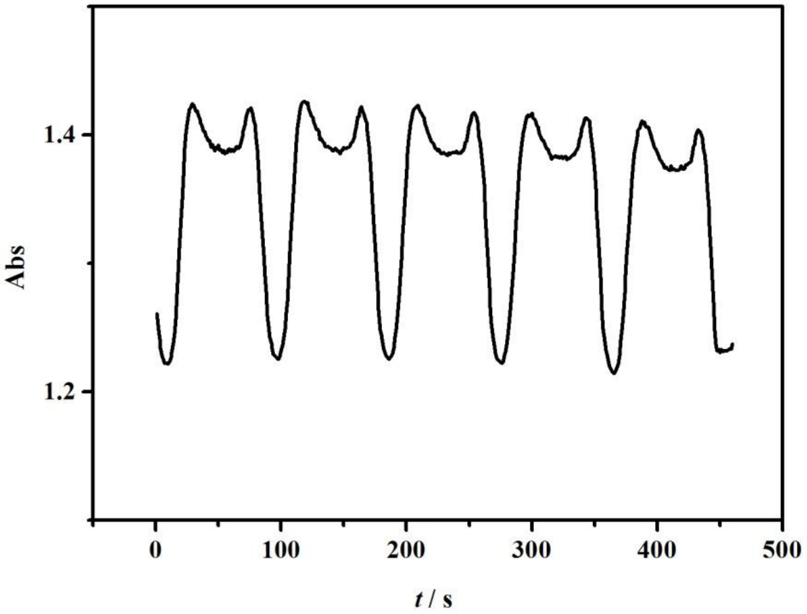


Figure 6. Ultraviolet absorption spectra of PANI/ITO electrode in 1mol/L H_2SO_4 solution at CV, λ=800nm,n=5, scan range: -0.6V~1V, scan rate,100mV/s, n=5.

In order to determine the stability of PANI/ITO electrode, put the electrode into 1mol/L H_2SO_4 solution, then scanned by cyclic voltammetry. From the PANI film's cyclic voltammogram, a pair of differentiated redox peaks appeared in figure 5. During the consecutive CV scanning, the redox peak potential of PANI film did not shifted. Whereas, the activity of PANI film gradually reduced by repeated electro-oxidation process, for this reason, the redox peak current decreased.

Figure 6 shows the ultraviolet absorption spectra during the CV process, at the same time, PANI film occurred redox reaction and reversible electrochromic phenomenon. In the reversible electrochromic process, doping ions have not changed, absorption value of PANI film in the oxidation state was largely unchanged.

4. CONCLUSIONS

In summary, we employed electrochemical polymerize PANI film on the ITO electrode. During the CV process in H_2SO_4 electrolyte solution, it happened the reversible redox reaction on PANI film, along with the reversible electrochromic phenomenon at the same time. This paper make use of electrochromic character of PANI film to detect hydrogen phosphate ion successfully. There is a good linear relationship between the Abs of the doped PANI film and the concentration of doped hydrogen phosphate ion, the limit of detection could achieve 0.023mmol/L. The results show that PANI film had a good selectivity for the hydrogen phosphate ion. The PANI/ITO electrode has the advantages of process simple and low cost, so it can be widely used in anion detection.

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References

1. T. Kidosaki, S. Takase and Y. Shimizu, *J. Sensor Technol.*, 2 (2012) 95.
2. R. J. Williams, *Anal. Chem.*, 55 (1983) 851.
3. B. López-Ruiz, *J. Chromatography A*, 881 (2000) 607.
4. J. S. Fritz, D. T. Gjerde, *Ion Chromatography*, WILEY-VCH, 2009, Weinheim.
5. I. A. Azath, P. Suresh, K. Pitchumani, *Sensors and Actuators B: Chemical*, 155 (2011) 909.
6. R. Sakai , E. B. Barasa , N. Sakai , S. Sato , T. Satoh and T. Kakuchi, *Macromolecules*, 45 (2012) 8221.
7. R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Chem. Soc. Rev.*, 39 (2010) 3936.
8. W. W. Huang, X. D. Yu, H. Lin, H. K. Lin, *J. Inclusion Phenomena and Macrocyclic Chem.*, 69 (2011) 69.
9. C. Suksai, T. Tuntulani, *Chem. Soc. Rev.*, 32 (2003) 192.
10. S. Mizukami, T. Nagano, Y. Urano, A. Odani and K. Kikuchi, *J. Am. Chem. Soc.*, 124 (2002) 3920.

11. H. D. P. Ali, P. E. Kruger and T. Gunnlaugsson, *New J. Chem.*, 32 (2008) 1153.
12. X. Y. Zhao, Y. Liu and K. S. Schanze, *Chem. Commun.*, 0 (2007) 2914.
13. J. C. Lacroix, K. K. Kanazawa and A. Diaz, *J. Electrochem. Soc.*, 136 (1989) 1308.
14. E. A. R. Duek, M. A. De Paoli and M. Mastragostino, *Adv. Mater.*, 4 (1992) 287.
15. D. Schlettwein, D. Wöhrle and N. I. Jaeger, *J. Electrochem. Soc.*, 136 (1989) 2882.
16. X. F. Kang, Y. D. Jin, G. J. Cheng and S. J. Dong, *Langmuir*, 18 (2002) 10305.
17. L. Zhao, L. Zhao, Y. X. Xu, T. F. Qiu, L. J. Zhi and G. Q. Shi, *Electrochim. Acta*, 55 (2009) 491.
18. Q. L. Hao, W. Lei, X. F. Xia, Z. Z. Yan, X. J. Yang, L. D. Lu and X. Wang, *Electrochim. Acta*, 55 (2010) 632.
19. Y. Liu, J. Lynch, *Proceedings of SPIE*, 7983 (2011) 798315/1.
20. Y. H. Chen, J. Y. Wu and Y. C. Chung, *Biosens. Bioelectron.*, 22 (2006) 489.