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Electrosynthesis of polypyrrole/sulfonated polyaniline composite films and their applications for ammonia gas sensing

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Abstract

Polypyrrole/sulfonated polyaniline (PPY/SPANI) composite films have been prepared by direct electrochemical polymerization of pyrrole in an aqueous solution of SPANI. Spectroscopic results demonstrated that the polyanion, SPANI, was incorporated into the PPY matrix as a dopant. The composite films exhibited a higher thermal stability than that of pure PPY. Scanning electron microscopic images revealed that the composite film had smooth and compact morphology. Furthermore, a simple ammonia sensing device based on the composite film showed high sensitivity and a low limit of detection.

Keywords: Polypyrrole; Sulfonated polyaniline; Composite

1. Introduction

Polypyrrole (PPY) is one of the most widely studied conducting polymers [1–3], mainly due to its high conductivity, good environmental stability and biocompatibility. PPY has been used in batteries [4], supercapacitors [5], sensors [6], actuators [7] and corrosion protections [8]. Up to now, PPY has been synthesized through a chemical or an electrochemical route, and its properties strongly depend on the conditions of syntheses [9]. In previous researches, most PPY films were doped with small inorganic anions such as Cl^- and ClO_4^-. These small counter ions can be incorporated (on oxidation) and ejected (on reduction) from the PPY film, and the film exhibits reversible redox characters [10]. In the last decades, a series of dopants have been investigated to improve the mechanical property, conductivity and stability of the resulting PPY [11,12]. Many bulky sulfonates including alkyl benzenesulfonate [13], pyrenesulfonate [14] and polyanions such as polystyrene sulfonate (PSS) were also used as the dopants [15]. Incorporating bulky anions into PPY films was reported to be an effective method for improving the environmental stability of PPY [13,16], and bringing it with special electrochemical properties. Only part of the anions in polyanions acted as the counter ions of PPY, leaving excess acidic groups for interaction with basic gases [17]. Therefore, the basic gas sensors based on PPY films doped with polyanions are expected to have improved performance.

Polyaniline (PANI) was another extensively studied conducting polymer which has high stability, good conductivity and reversible redox property. Sulfonated polyaniline (SPANI) has sulfonic groups on its backbones, so it is soluble in water [18–20]. SPANI with methoxyls on its benzene rings has been used as the dopant for PPY and the resulting composite film exhibited improved cathodic expansions [21–23]. Herein, we report the syntheses and characterizations of PPY/SPANI self-standing films by direct oxidation of pyrrole in the aqueous solution of SPANI. These films showed unique electrochemical properties and high performance on ammonia gas sensing.

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2. Experimental

2.1. Materials

Aniline and pyrrole (analytical pure grade) were purchased from Sinopharm Chem. Reagent Co. Ltd (Beijing, China) and distilled under reduced pressure before use. Ammonium persulfate and chlorosulfonic acid were bought from Beijing Chem. Reagent Co. (Beijing, China) and were used without further purification.

2.2. Synthesis of PPY/SPANI composite film

PANI (in emeraldine form) was synthesized by chemical oxidation of aniline with ammonium persulfate at 0 °C [24]. PANI was sulfonated with chlorosulfonic acid and finally hydrolyzed into SPANI [20]. The electropolymerization was carried out at room temperature in one compartment cell using a 273A potentiostat (EG&G Princeton Research, USA). The working electrode was an indium tin oxide (ITO) glass sheet with surface area of 2 cm × 1 cm and a platinum sheet was used as the counter electrode. The working electrode used to study the electrochemical property of the film was a gold-covered quartz plate with an efficient area of 0.82 cm^2. The typical electrolyte was an aqueous solution of 0.1 $mol\,L^{-1}$ pyrrole containing 0.1 $mol\,L^{-1}$ repeat units of SPANI (pH ∼1.7). The electrolytes were deoxygenated by bubbling dry nitrogen gas. All the potentials were referred to an Ag/AgCl electrode immersed in the solutions directly. PPY/SPANI composite films were electropolymerized potentiostatically at 0.6 V or by cyclic potential scanning in the range of −0.8 to 0.8 V at a scan rate of 100 $mV\,s^{-1}$. PPY film doped with ClO_4^- (PPY/ClO_4^-) was also synthesized under the same conditions except the electrolyte was an aqueous solution of 0.1 $mol\,L^{-1}$ pyrrole containing 0.1 $mol\,L^{-1}$ $LiClO_4$.

2.3. Characterizations

Raman spectra were obtained on a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) employing a 633-nm laser beam, and a charge coupled device detector with 4-cm^{-1} resolution. The spectra were recorded by focusing a 1−2 μm laser spot on the sample with a 20× objective and accumulated three times for 30 s each. IR spectra were carried out using a GX Fourier transform infrared (FTIR) spectrometer (Perkin Elmer) with KBr pellets of the composites. The morphologies of the composites were studied by using a scanning electron microscope (KYKY 2800, China), operated at 25 kV. Electrochemical examinations were performed on a 273A potentiostat (EG&G) under computer control, and the weight changes of a PPY film during its redox process were studied by using a 440 A time-resolved electrochemical quartz crystal microbalance (CHI, USA). Elemental analysis was carried out on a CE-400 elemental analyzer (EAI, USA). X-ray photoelectron spectra (XPS) were taken out by a PHI Quantera SXM X-ray photoelectron spectrometer (Perkin Elmer).

2.4. Fabrication and test of ammonia sensors

The ammonia sensing performance was studied by measuring electric resistance changes of the PPY/SPANI beam in the gas flow of ammonia/nitrogen using two-electrode method. The configuration of the device is illustrated in Fig. 1a. A piece of PPY/SPANI (or PPY/ClO_4^-) beam (approximately 2 mm × 5 mm × 10 μm) was fixed onto two patterned ITO electrodes with a gap of 1.5 mm. Conductive carbon print (SPI Supplies, USA) was applied to adhere the PPY film onto the ITO electrodes and to reduce the contact resistances. These two ITO electrodes were connected to a potentiostat under computer control. The current signal was recorded by applying a constant voltage between these two electrodes.

The concentration of ammonia was controlled by a mass flow controller (MFC) model D07-12 (Sevenstar Huachuang Electronics Co. Ltd, China). The total flow was 1000 sccm (standard cubic centimeter per minute), and the ammonia concentration was modulated to be 20, 40, 60 or 80 ppm by mixing 1000 ppm source ammonia gas with nitrogen flow under MFC control. The mixed gas was led to a glass chamber with a volume of 500 mL in which the sensing device was fixed (Fig. 1b). Ammonia gas was 1 min on and then cut off to leave the device under nitrogen flow until the current of the device recovered to its original value. The response was defined by the slope of the current−time curve recorded during the period of 20−40 s after ammonia was on; it was calculated in Ampere per second.

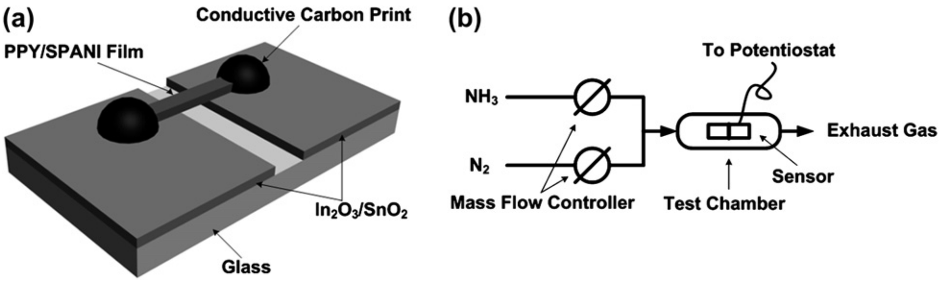

Fig. 1. Sketch of the sensor structure (a) and test system (b).

3. Results and discussion

Fig. 2 shows the cyclic voltammograms (CVs) of 0.1 mol L^{-1} pyrrole in the aqueous solution containing 0.1 mol L^{-1} SPANI units. It is clear from this figure that each CV cycle has two couples of redox waves. A regular increase of anodic and cathodic currents of the redox waves indicated the growth of an electroactive polymer film on the working electrode, and the equal gaps between neighboring cycles implied that the growing film had good conductivity. The CV curve of pyrrole in the aqueous solution of an electrochemically inert polyanion (e.g. PSSA) showed only one couple of redox waves of PPY (Fig. S1). Therefore, the two couples of redox waves shown in Fig. 2 are attributed to SPANI and PPY, respectively. It is believed that the large polyanion such as SPANI in PPY is difficult to be removed from the film. Therefore, only H$^+$ ions were involved in the redox process; this process usually occurs at relatively low potentials (−0.4 V and ∼0.2 V) [13]. SPANI shows more reversible redox waves in acidic solution than in a basic medium, and the wave potentials shifted to lower potentials with the increase of pH value of the medium. Thus, the redox waves at around 0.1 V are due to the trap and ejection of H$^+$ ions during the redox processes [25]. The CV of SPANI aqueous solution also showed these redox waves (Fig. S2). The electrochemical results described above indicate that SPANI is a good supporting electrolyte for electrochemical polymerization of pyrrole.

The cyclic voltammograms of the composite film are demonstrated in Fig. 3 (for comparison, the CV of PPY doped with PSSA is shown in Fig. S3). The first oxidation wave at about −0.4 V was attributed to the ejection of cations from the film, which can be confirmed by the increase of EQCM frequency, corresponding to a decrease of PPY film mass (Fig. 3) [13]. This process usually occurs in the cases of PPY doped with bulky dopants and at low potentials. The corresponding reduction wave resulted in entrapping cations into the film, displaying a frequency decrease in the EQCM trace. The weak oxidation peak at about 0.5 V is associated with cation doping as the charge number on the polymer chains exceeds the number of bound residual anions. This fact was confirmed by the EQCM curve, showing a sharp increase of electrode mass [13]. The redox waves at about 0 V are associated to SPANI, because the redox waves of SPANI are shifted to lower potentials with the increase of the pH value of the medium, and appeared at around 0 V in a neutral solution [25].

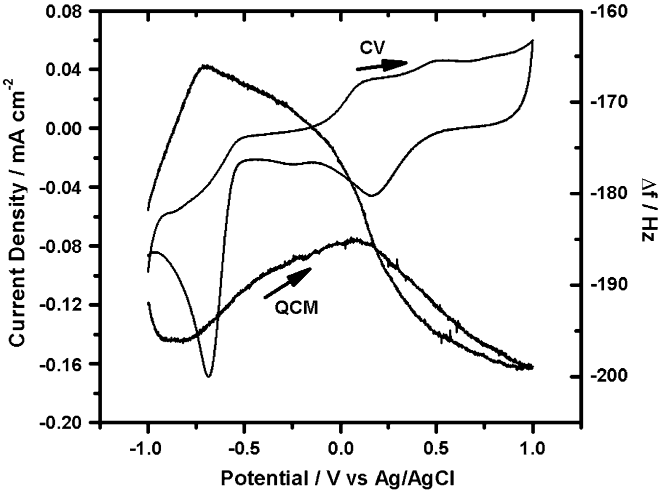

Fig. 3. Cyclic voltammogram and QCM curves of a PPY/SPANI film (electrochemically deposited at 0.7 V) on a gold-coated quartz crystal electrode in an aqueous solution containing 0.1 mol L^{-1} $LiClO_4$ at a scan rate of 50 mV s^{-1}.

Elemental analysis examination results indicated that pure SPANI contained 35.45 wt% carbon, 3.56 wt% hydrogen, 7.02 wt% nitrogen and 13.43 wt% sulfur. Accordingly, the sulfonation degree of SPANI was calculated to be 0.85. The nitrogen to sulfur atomic ratio (N/S) of the composite was measured by XPS to be approximately 2.3:1.0 (Fig. S4). Thus, the ratio of PPY to SPANI repeat units in the composite was calculated to be about 1:1. PPY was believed to have the highest doping level of 0.33, so at least, 67% $-SO_3H$ groups

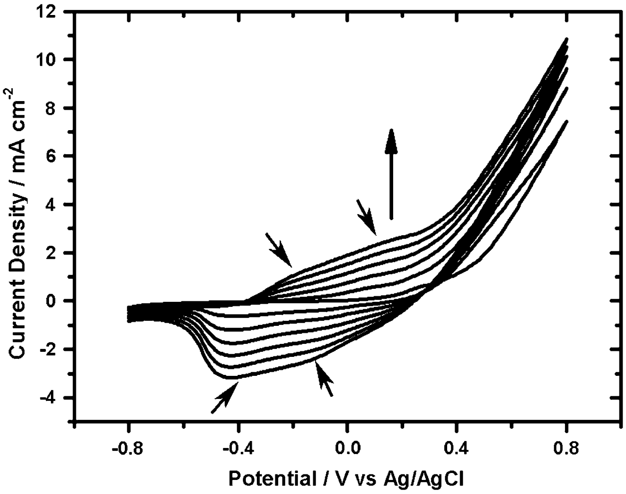

Fig. 2. Cyclic voltammograms of 0.1 mol L^{-1} pyrrole in an aqueous solution containing 0.1 mol L^{-1} repeat units of SPANI at a scan rate of 100 mV s^{-1}. Four short arrows indicate the redox waves.

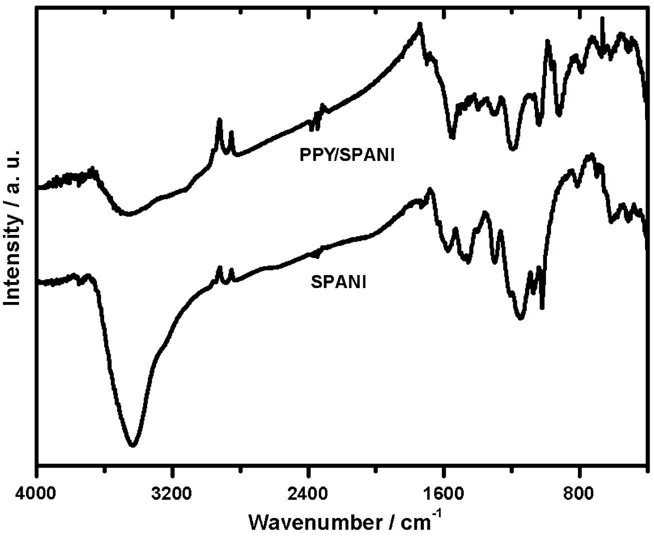

Fig. 4. FT-infrared spectra of SPANI and a PPY/SPANI composite film electrosynthesized at a constant potential of 0.7 V.

of SPANI were in dissociated states. These groups may help in absorbing ammonia gas as the film was applied for fabricating ammonia sensors.

Fig. 4 shows the FT-infrared spectra of SPANI and PPY/SPANI composite films. In the spectrum of the composite, the characteristic band related to S–O bond stretching of SO_3^- groups appeared at 1023 cm^{-1}, indicating that SPANI was incorporated into the film [26]. The bands around 1700 cm^{-1} are weak, implying that the PPY film is scarcely over-oxidized during the course of polymerization. Fig. 5 shows the Raman spectra of SPANI and PPY/SPANI composite films. The spectrum of the composite film shows characteristic features of doped PPY [27–29]. The strong band at 1600 cm^{-1} is assigned to the stretching vibration of C=C bonds of PPY. The double peaks at about 1048 and 1085 cm^{-1} are assigned to the C–H in-plane deformation; the other double peaks at about 1334 and 1373 cm^{-1} are attributed to the ring stretching modes of PPY. The bands at 983 and 934 cm^{-1} are assigned to the ring deformation associated with polaron and bipolaron, respectively; the intensity of the latter band is much stronger than that of the former, implying a high doping level of the PPY composite film. The conductivity of the film was measured to be 10^{-1} to 10^{0}. Since there was no other dopant except SPANI anions, it is reasonable to conclude that the PPY film was doped by SPANI.

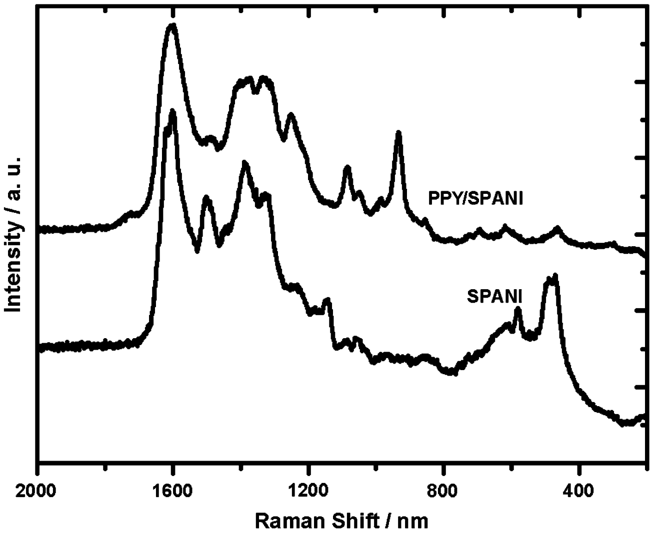

Fig. 5. Raman spectra of PANI and a PPY/SPANI composite film electrosynthesized at a constant potential of 0.7 V.

The as-prepared wet composite film is flexible and shiny. The SEM images shown in Fig. 6 indicate that the two surfaces of the resulting films are smooth and compact. This morphology is similar to that of the PPY film electropolymerized in an aqueous solution of other polyanions, such as PSS salt [15,30]. The long molecular chains of SPANI played an important role in the film growth process: they can catch the soluble oligopyrrole by sulfonic group and fix them on the

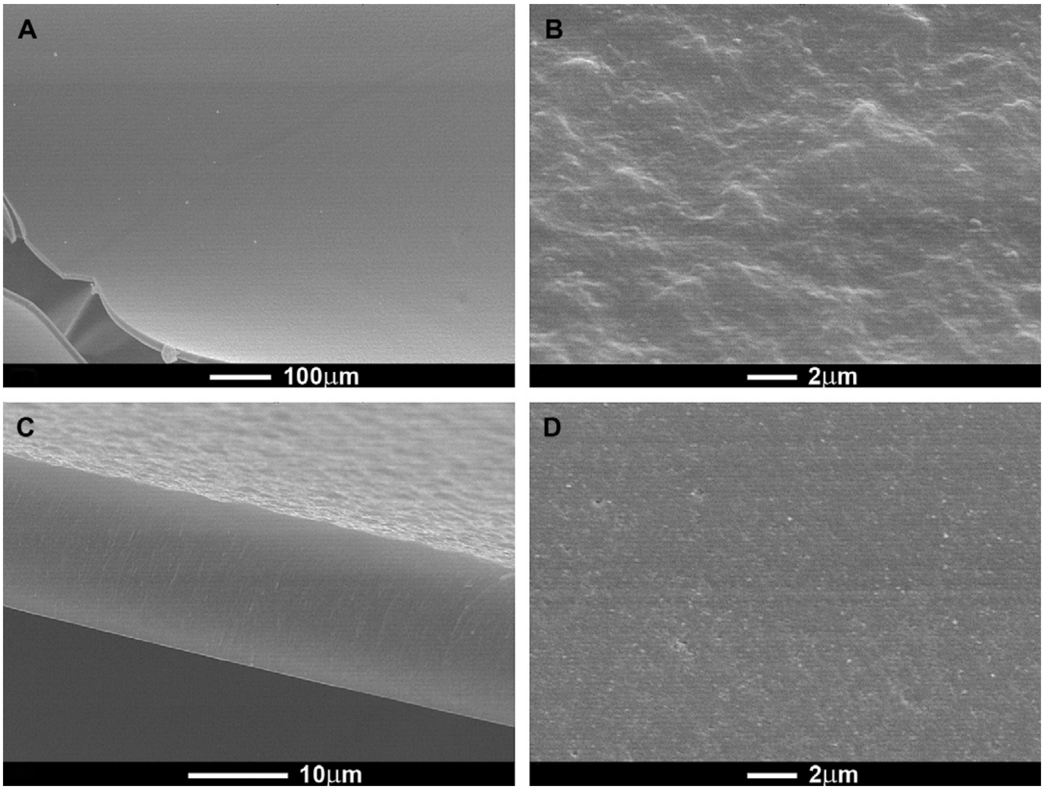

Fig. 6. SEM images of PPY/SPANI composite film synthesized by electrolysis of 0.1 mol L^{-1} pyrrole in an aqueous solution containing 0.1 mol L^{-1} repeat units of SPANI at a constant applied potential of 0.7 V. (A and B) The surface in contact with the electrolyte; (C) cross-section; (D) the surface in contact with the electrode.

surface of the film, which leads to the formation of a compact and smooth film [30].

Fig. 7 presents the TGA curve of the PPY/SPANI composite film. According to this curve, the composite film contained about 10% water by weight, due to the strong interaction between water and SPANI. The decomposition temperature of the film was measured to be approximately 250 °C, which is slightly higher than that of ClO_4^- doped PPY (~200 °C) [11]. This is possibly due to the strong interactions between polyanions and PPY chains.

Fig. 8 illustrates the electric resistance changes of the films as a function of exposure time in ammonia gas. These curves were recorded based on the devices depicted in Fig. 1. The electrical conductivities of the sensing films decreased when the film was exposed to ammonia gas. This is mainly due to the fact that electron donating ammonia reduced the charge carrier density of PPY. As can be seen from Fig. 8, the PPY/SPANI composite film shows higher response to ammonia than that of a PPY film doped with ClO_4^- under the same condition of test. This result indicated that the SPANI component in the composite film is also involved in the sensing process. In fact, SPANI is sensitive to ammonia by deprotonation, which resulted in decreasing the conductivity of SPANI. Furthermore, the introduction of SPANI into the PPY film alters the partition coefficient between gas phase and polymer phase [17,31]. Excess $-SO_3H$ groups on SPANI can help PPY composite film to absorb more ammonia, and then more PPY component was reduced to produce stronger response.

Fig. 9 illustrates the response of the sensing devices based on PPY/SPANI composite film to different concentrations of ammonia. In our experiment, the reaction between PPY and ammonia did not reach equilibrium in the initial several minutes, however, the current dropped down almost linearly (relation coefficient >0.999 in the region of 20–40 s), indicating a high reaction rate. Obviously, the slope of the current dropping line was related to reaction rate, and also found to have linear relationship with the concentration of ammonia, as shown in Fig. 9b. These results indicated that the PPY/SPANI composite film can be used for detecting ammonia gas with

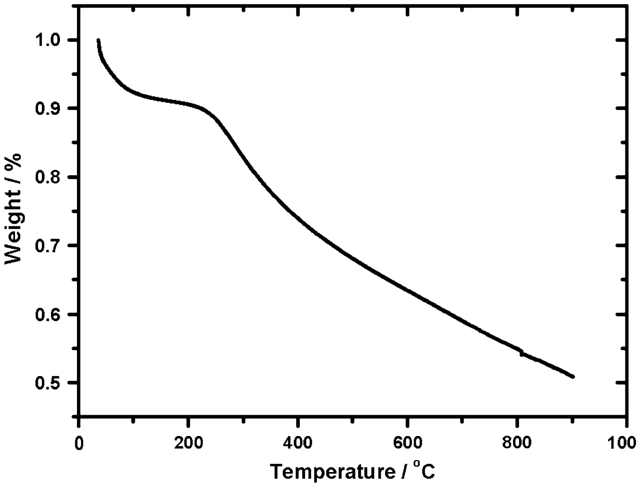

Fig. 7. TGA curve of the composite film shown in Fig. 6 under nitrogen atmosphere.

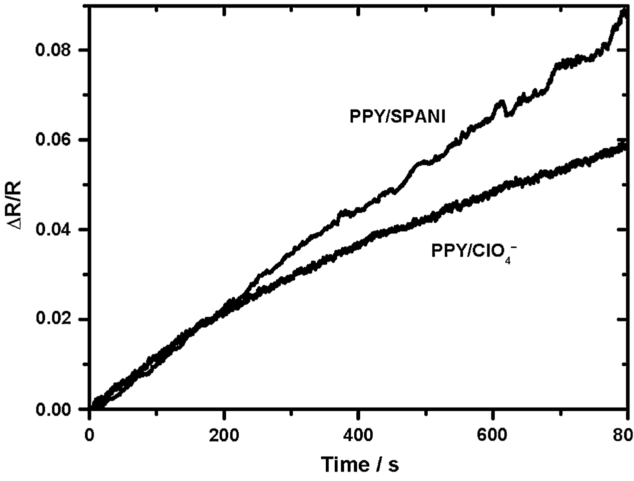

Fig. 8. Responses of the sensing devices based on the PPY/SPANI composite film shown in Fig. 3, or on a ClO_4^- doped PPY with the same thickness to 25 ppm ammonia.

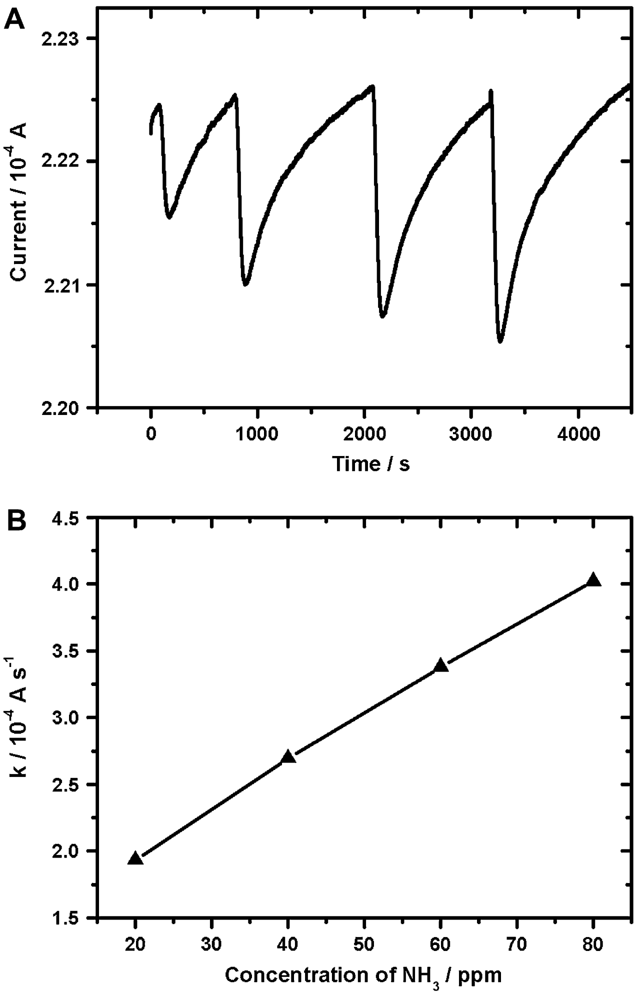

Fig. 9. (A) Response characteristic to ammonia of sensing device based on the PPY/SPANI composite film shown in Fig. 3 (the applied potential was 2 V); (B) plot of the slope of current dropping line vs. ammonia concentration.

concentrations of tens of parts per million. The limit of detection was tested to be lower than 15 ppm based on the simple sensor configuration.

4. Conclusions

PPY/SPANI composite films can be electrosynthesized in an aqueous solution of sulfonated polyaniline. These films showed electrochemical properties of both PPY and SPANI. They have smooth surface, compact structure and good thermal stability. The simple sensing device based on the composite film can accurately detect ammonia gas with a limit of detection lower than 15 ppm. Their sensitivity is higher than that of the devices based on PPY films doped with small anions such as ClO_4^-.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2007.05.033.

References

[1] Zhang XY, Manohar SK. J Am Chem Soc 2006;127:14156.
[2] Petitjean J, Aeiyach S, Lacroix JC, Lacaze PC. J Electroanal Chem 1999;478:92.
[3] Chen GZ, Shaffer MSP, Coleby D, Dixon G, Zhou WZ, Fray DJ, et al. Adv Mater 2000;12:522.
[4] Killian JG, Coffey BM, Gao F, Poehler TO, Searson PC. J Electrochem Soc 1996;142:936.
[5] Jurewicz K, Delpeux S, Bertagna V, Beguin F, Frackowiak E. Chem Phys Lett 2001;347:36.
[6] Bai H, Shi GQ. Sensors 2007;7:267.
[7] Han GY, Shi GQ. Sens Actuators B 2006;113:259.
[8] Truong VT, Lai PK, Moore BT, Muscat RF, Russo MS. Synth Met 2000;110:7.
[9] Kuhn HH, Child AD, Kimbrell WC. Synth Met 1995;71:2139.
[10] Li YF, Qian RY. J Electroanal Chem 1993;362:267.
[11] Liu YC, Tsai CJ. J Chem Mater 2003;15:320.
[12] Yuan YJ, Adeloju SB, Wallace GG. Eur Polym J 1999;35:1761.
[13] Bay L, Mogensen N, Skaarup S, Sommer-Larsen P, Jørgensen M, West K. Macromolecules 2002;35:9345.
[14] Lu GW, Li C, Shi GQ. Polymer 2006;47:1778.
[15] Qu LT, Shi GQ, Liu C, Yuan JY, Qian WB. Chin J Polym Sci 2005;23:37.
[16] Ricks-Laskoski HL, Buckley LJ. Synth Met 1995;156:417.
[17] Hwang BJ, Yang JY, Lin CW. J Electrochem Soc 1999;146:1231.
[18] Shimizu S, Saitoh T, Uzawa M, Yuasa M, Yano K, Maruyama T, et al. Synth Met 1997;85:1337.
[19] Chen SA, Hwang GW. Macromolecules 1996;29:3950.
[20] Ito S, Murata K, Teshima S, Aizawa R, Asako Y, Takahashi K, et al. Synth Met 1998;96:161.
[21] Zhao HJ, Wallace GG. Polym Gels Networks 1998;6:233.
[22] Tanaka A, Takashima W, Kaneto K. Chem Lett 2004;33:1470.
[23] Tanaka A, Takashima W, Kaneto K. Thin Solid Films 2006;499:179.
[24] Adams PN, Laughlin PJ, Monkman AP, Kenwright AM. Polymer 1996;37:3411.
[25] Yue J, Wang ZH, Cromack KR, Epstein AJ, MacDiarmid AG. J Am Chem Soc 1991;113:2663.
[26] Yang YS, Wan MX. J Mater Chem 2001;11:2022.
[27] Furukawa Y, Tazawa S, Fujii Y, Harada I. Synth Met 1988;24:329.
[28] Liu YC, Hwang BJ. Synth Met 2000;113:203.
[29] Chen FE, Zhang JX, Wang F, Shi GQ. J Appl Polym Sci 2003;89:3390.
[30] Momma T, Nishimura K, Osaka T, Kondo N, Nakamura S. J Electrochem Soc 1994;141:2326.
[31] Bissell RA, Persaud KC, Travers P. Phys Chem Chem Phys 2002;4:3482.