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Oxidative polymerization of pyrrole in the presence of a poly (sodium-p-styrenesulfonate) and its gas-responses

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Abstract To overcome the problem of film-forming technology, water-soluble polypyrrole was obtained in the process of chemical oxide by adding a small amount of poly (sodium-p-styrenesulfonate). The resulting product PPy/Poly(sodium-p-styrene sulfonat) was coated on the interdigital electrodes of carbon via spin-coating or casting approach, and its gas-sensitivity to trimethylamine at room temperature was investigated. The results indicated that, the technology of film-forming was not only improved greatly, but also this film still showed good gas-sensitivity to trimethylamine of 3.189×10^{-1} mol/m^3, its value of gas-sensitivity had reached to 2–3 orders of magnitude within 3 min, had good selectivity to analogy gases, and its resistance to moisture was improved obviously. Otherwise, this film also exhibited good reproducibility and stability, and easily recovered with high-purity N_2 at room temperature.

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Introduction

Because of its mechanical flexibility, environmental stability, and controllable conductivity with doping/undoping, conductive polymers have a lot of potential applications in many fields, such as light-weighted battery electrode, electromagnetic shielding device, anticorrosion coatings, chemical sensors, biological sensors and so on [1–3].

Polypyrrole is one of the typical conductive polymers, and also is one kind of sensitive materials at or near room temperature operating, and has a convenient operating and attractive prospect of development in the fields of sensors.

Currently, the study on polypyrrole is still one of the hot fields, one of the main reason is that devices with excellent properties would be expected to be obtained via tailoring the nano-structure of conductive polymer with template, non-template and seeding approach [1–5]. The other emphasis is focusing on the improving the solubility of polypyrrole.

Due to the poor solubility of polypyrrole, it is difficult to form film with general method, whereas some modifications of polypyrrole would affect its properties much. The electropolymerization is a reasonable approach to prepare film, and has been widely used to fabricate the biological sensors, but it is very difficult to carry out on the interdigital electrodes. To solve these problems, Song and co-workers [6] prepared and characterized the soluble polypyrrole, and obtained good preliminary results. Sarac and co-workers [7, 8] had carried out the oxidative polymerization of pyrrole in the presence of a polyanion, and obtained water-soluble polypyrrole interpolymer complex. To improve the technology of film-forming of polypyrrole and avoid air pollution caused by organic solvent, and basing on the in-situ doping feature of polypyrrole, we obtained water-soluble polypyrrole via inducement effects by adding a small amount of poly (sodium-p-styrenesulfonate), and examined its gas-responses.

So far, although most of researches on conductive polymer is still focusing on the preparation of materials and morphology characterization [1–3, 5, 6], a very few reports touched upon the properties of device. According to the data of published, the properties are mostly still quite low, and the response rate is very slow [9]. In our opinion, there are two main problems obstruct the development progress. One is that there are too many techniques involved from the functional material to the device fabrication, and some of them are difficult to overcome in near future. The other is that the conductivity of polypyrrole strongly depends upon the doping and undoping. Because there are so many factors affecting on the properties of devices and it is too difficult to achieve the effect of doping in-situ polymerization using common doping method, the excellent properties of the material are not easy to be realized on the devices. Otherwise, the contacts of electrodes are also important factors for improving the properties of device. Consequently, how to obtain the measure physical signal via a simple approach is very important for sensor applications.

Recently, Huang and co-workers [10–12] had investigated the sensitive properties of sensors based on nanostructured polyaniline prepared with interface polymerization and interdigital gold electrodes to obtain good results, which encourage us to develop organic sensors with high sensitivity via other approaches.

Otherwise, trimethylamine is one of the important organic ammonia, which is produced with metabolism process of organs of animal and protein. And it is important one of the toxic gases in biology field and foodstuff industry. At present, it is usually determined with sensor of metal oxide mostly, which has low gas-sensitivity, and needs to operate at high temperature. To improve its sensitivity and response speed, the gas-sensitivity examination was carried out with polypyrrole film in our experiments.

To obtain a film sensor with high-sensitivity, rapid response, low-cost, reversible at room temperature and convenient operating, we had ever studied a series of organic film sensor [13–15], and obtained some good results. Herein, this paper will introduce the preparation of polypyrrole based sensor via a improving its film-forming technology.

Experimental

Materials

Pyrrole (AR) was freshly distilled in vacuum prior to use, ammonium peroxydisulfate (AR), hydrochloride (AR), poly (sodium-p-styrenesulfonate) (the average molecular weight of poly(sodium-p-styrene sulfonat) is 70000) are commercially available. Deionized filtered water was used in all studies.

The electrode with a 0.5 mm gap and a 1 mm length is made of carbon paste, which is prepared with screen-printing technology, the substrate of electrode is polypropylene plate with 0.5 mm thickness.

Preparation of sensing film

The coating mixture was prepared by adding pyrrole and ammonium peroxydisulfate (mol ratio is 1:2) in hydrochloride solution, and a small amount of poly (sodium-p-styrenesulfonate) was added. The molar concentration of pyrrole, hydrochloride and poly (sodium-p-styrenesulfonate) is 0.015 M, 0.015 M, 2.86×10^{-4} M respectively. A black solution of water-soluble polypyrrole was obtained after standing 24 h. The gas-sensor was fabricated via carbon electrode being immerged in the mentioned mixture, or with spin-coating method or casting approach, and dried at room temperature.

Gas-response characterization of sensor

The gas-response characterization of sensor to vapor was same as the reference [13, 16]. The details of procedure are described as follows. The device was put into an airproof test box (2.5 L), which was connected with vacuum and high purity N_2 system with three-way valves. While 10 volts DC voltage was applied on the interdigital electrodes, the response DC current was measured using Keithley 236 Source Measure Unit. The DC current was measured continuously under N_2 atmosphere with arbitrary time interval, such as 1 sec for evaluating programmed detection time, and the current value was recorded automatically by an IMB PC compatible computer. The test box was flushed with high purity N_2 repeatedly, and till the current slowly reached the steady value and kept invariableness. At this moment, a certain amount of trimethylamine or other volatile solvent (such as $0.2 \times 10^{-6} m^3$) was injected into the test chamber with a syringe. Definition of gas-sensitivity(R) of the film is the ratio of I_{gas}/I_{N2}, where, I_{gas} and I_{N2} is the current of sensor on exposure to measured gas and N_2 respectively.

The FTIR spectra measurement

The FTIR spectra were taken in silicon wafer, and recorded on an IFS 66 V/S Fourier Transform Infrared Spectrometer made in Bruker Company. The water-soluble polypyrrole was coated on the surface of silicon wafer, dried at room temperature, then for determination. Comparison experiment was carried out with polypyrrole in-situ polymerization on the surface of silicon wafer.

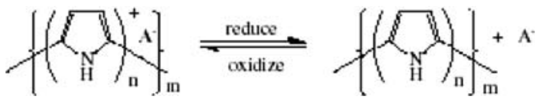
The UV-vis absorption of film measurement

The UV-vis absorption was recorded by a CARY Bio100 spectrophotometer. The water-soluble polypyrrole was coated on the quartz glass, and then dried at room temperature for determination.

Results and discussion

FTIR spectra of polypyrrole composite film

Due to the existence of nitrogen (N) atom of polypyrrole, in an acid media, it is very easy for protonation, which the positive charge has been delocalized in the whole molecule π-conjugation structure of polypyrrole, and then led to the formation of ion pair with some anions. Because the redox of polypyrrole is a reversible process. Consequently, polypyrrole can be easily doped with a large number of anions, including polyanion and even living cells. See the Scheme 1.



Scheme 1 The reversible process of redox of polypyrrole

Basing on the doping feature of polypyrrole, the solubility of polypyrrole would be improved greatly via utilizing several soluble polyanions.

Poly (sodium-p-styrenesulfonate) is a typical of water-soluble polymer, and also a polyanion. With aid of the inducement effects of sulfonate group of the poly (sodium-p-styrenesulfonate) molecule, the solubility of polypyrrole would also be improved at certain extent according to the needs of different applications. In the comparison experiments under similar conditions, we obtained precipitation of polypyrrole without adding poly (sodium-p-styrenesulfonate), and for the system of adding small mount of poly (sodium-p-styrenesulfonate) (about 4.29×10^{-4} M), we obtained a black solution of water-soluble polypyrrole. But, when the adding contents of poly (sodium-p-styrene-sulfonate) was decreased further to 4.29×10^{-4} M, 2.86×10^{-4} M, 2.28×10^{-4} M respectively, although water-soluble polypyrrole in macroscopic state was also obtained, the precipitation would be observed in the storing for a long time. But this would not affect the preparation of device, it may adjust the adding contents of poly (sodium-p-styrenesulfonate) at will according to the needs of different applications of sensor. This illustrated that the ''soluble'' of polypyrrole pointed in the paper maybe be not really soluble. It is possibly stable colloidal suspensions, and the stable time strongly depended upon the contents of poly(sodium-p-styrene sulfonat) added. Otherwise, in our experiments, it is found that no precipitation was appeared even in the storing for one year when the adding contents of poly (sodium-p-styrenesulfonate) was 4.29×10^{-4} M.

The FTIR spectra of polypyrrole film in our experiments was shown in Fig. 1.

Figure 1 shows that, 3,248 cm^{-1} is attributed to the stretching peak of N-H, 1450 cm^{-1} is to the stretching peak of C–N. This illustrated that this sensitive film contained polypyrrole. Because the mount of poly (sodium-p-styrenesulfonate) added in our experiment was very small, no obvious difference was observed from the FTIR spectra of polypyrrole film with and without poly (sodium-p-styrenesulfonate). Otherwise, since the polypyrrole is easily prepared with chemical oxide method, and large literatures have reported its synthesis and characterization. Herein, the details were no longer discussed in this paper. Therefore, despite the solubility of polypyrrole was increased greatly by the adding a small amount of poly (sodium-p-styrenesulfonate), but its effects to major components were a very little.

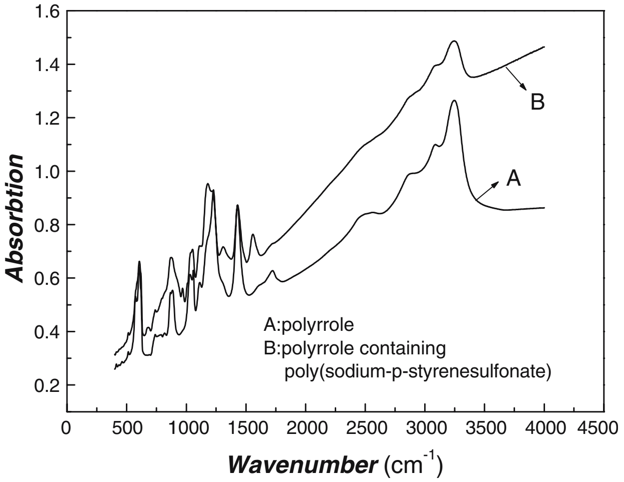


Fig. 1 FTIR spectra of the resulting product PPy/ Poly(sodium-p-styrene sulfonat)

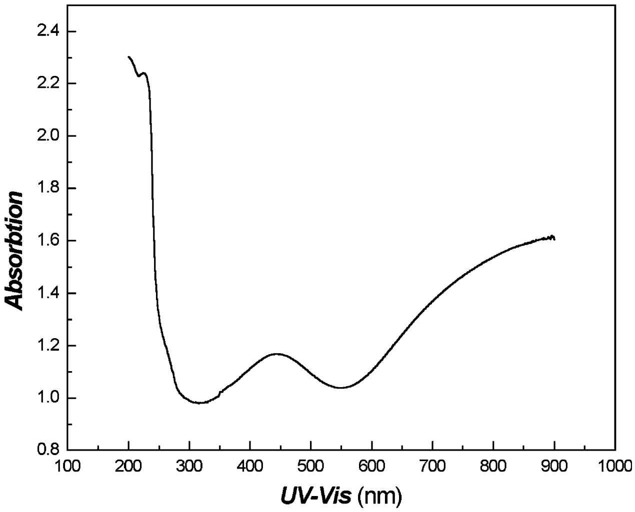


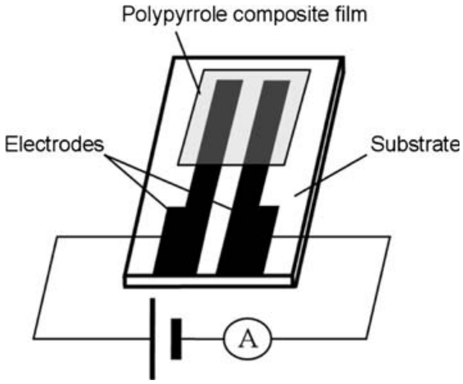
Fig. 2 UV-vis spectra of the resulting product PPy/ Poly (sodium-p-styrene sulfonat)

The UV-vis spectra of polypyrrole film in our experiments was shown in Fig. 2.

Figure 2 shows that, the strong absorption peak near 440 nm, 901 nm were observed, it was attributed to the absorption of π-polaron, bipolaron respectively. These are good agreements with the literatures [10].

Gas-response of polypyrrole film in our experiments to trimethylamine

The structure of sensor was illustrated in Scheme 2 [12].



Scheme 2 The structure of sensor in our experiments

It is well known that polypyrrole is one of important electroactive materials. When the voltage was applied on, the absorption ability of polypyrrole film to vapors was increased obviously. And according to the previous reports, although the separation of amino acids had been carried out based on the feature of weak interaction of polypyrrole with chromatographic technology, which acted as a stationary phase, some very similar amino acids can be identified. So, it is meaningful to obtain a measurable physical signal of sensor based on this weak interaction. In our experiments, the determination of gas-sensitivity of sensor is based on the electroactive feature of polypyrrole.

The gas-response of polypyrrole film to trimethylamine was shown in Fig. 3.

It is shown from Fig.3 that, the polypyrrole film to trimethylamine of 3.189×10^{-1}mol/m^3 has high gas-sensitivity and rapid response speed, it took about 200 s to reach 3 orders.

Moreover, another important property of sensor is reversibility. This property is also determined in our experiment. It is found that, the device could be recovered completely with high-purity N_2 at room temperature, and can be utilized repeatedly. The curve of desorption was shown in Fig. 4.

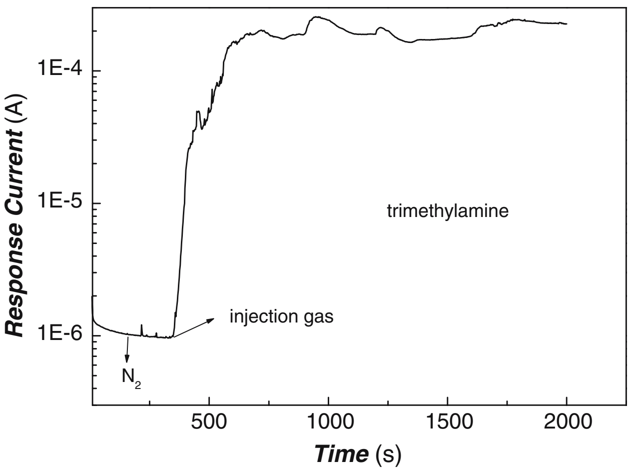


Fig. 3 Dependence of gas-response of the resulting product PPy/ Poly(sodium-p-styrene sulfonat) to trimethylamine (3.189×10^{-1} mol/m^3) on time

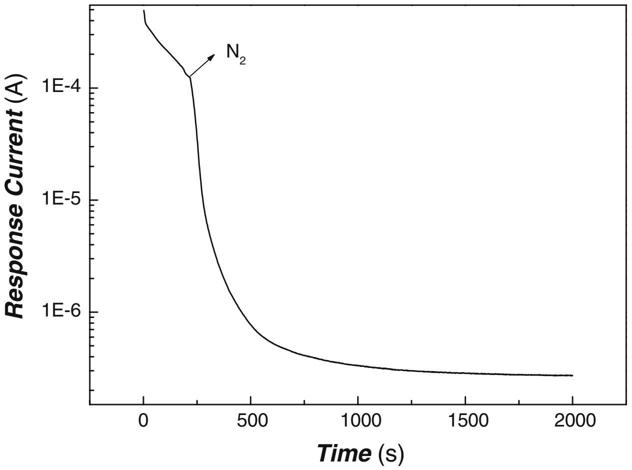


Fig. 4 Curve of desorption of the resulting product PPy/ Poly(sodium-p-styrene sulfonat) with high-purity N_2

Figure 4 shows that the sensor of polypyrrole has good reversibility.

The real mechanism of gas-sensitivity should be attributed to the interaction between the sensitive film and adsorbed gas molecular, which conclude strong interaction (chemical bond) and weak interaction (such as hydrogen bonding, van der Waals force, and so on.). For strong interaction system, its recovery is generally very difficult, and that for weak interaction system, its recovery is very easier at room temperature with high-purity N_2. Therefore, Fig. 4 illustrated that the physical adsorption took main roles in contribution to gas-sensitivity.

Gas-responses and selectivity of polypyrrole film in our experiments to analogy gases and interferent gases

Unlike enzyme sensors, normally a single chemical sensor has no specific character to distinguish gases although some gas sensor array can be used to identify different gases with aid of artificial neural network system. For this reason, the gas-responses of polypyrrole film to a series of vapors (trimethylamine, triethylamine, ammonia, formaldehyde, acetone, and alcohol) were examined under similar conditions. The results were shown in Fig. 5.

It is shown from Fig. 5 that, a distinct difference of gas-sensitivity and response rate to some similar vapors was observed. The value of gas-sensitivity and the response rate of triethylamine and ammonia are much lower than that of trimethylamine. At the same time, the gas-sensitivity to formaldehyde, acetone and alcohol are also far lower than that of trimethylamine. Consequently, this organic film sensor could distinguish the trimethylamine, triethylamine, ammonia, formaldehyde, acetone, alcohol and so on.

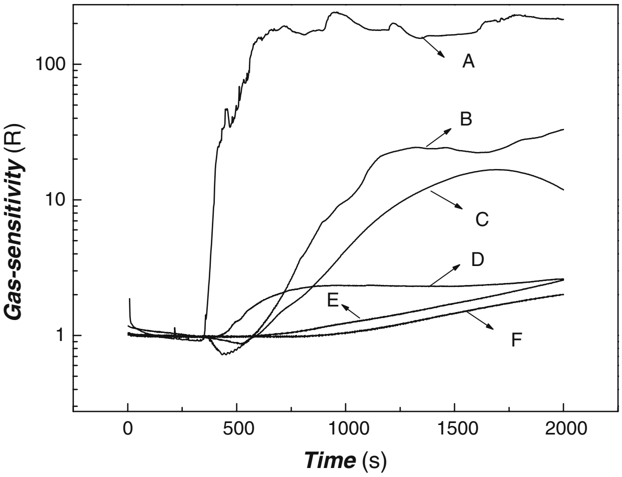


Fig. 5 Gas-responses of the resulting product PPy/ Poly(sodium-p-styrene sulfonat) to a series of vapors (A: trimethylamine; B: ammonia; C: triethylamine; D: formaldehyde; E: acetone; F: alcohol).

Effects of a small amount of poly (sodium-p-styrenesulfonate) on the gas-responses of polypyrrole film

The purpose of adding a small amount of poly (sodium-p-styrenesulfonate) is improving the solubility of polypyrrole, but whether does this bring some disadvantages for gas-sensitivity? To validate this problem, the comparison test of gas-response examination was carried out with insoluble polypyrrole in-situ polymerization under similar condition. The results were shown in Fig. 6.

Figure 6 shows that, although the gas-sensitivity of film was decreased greatly by adding a small amount of

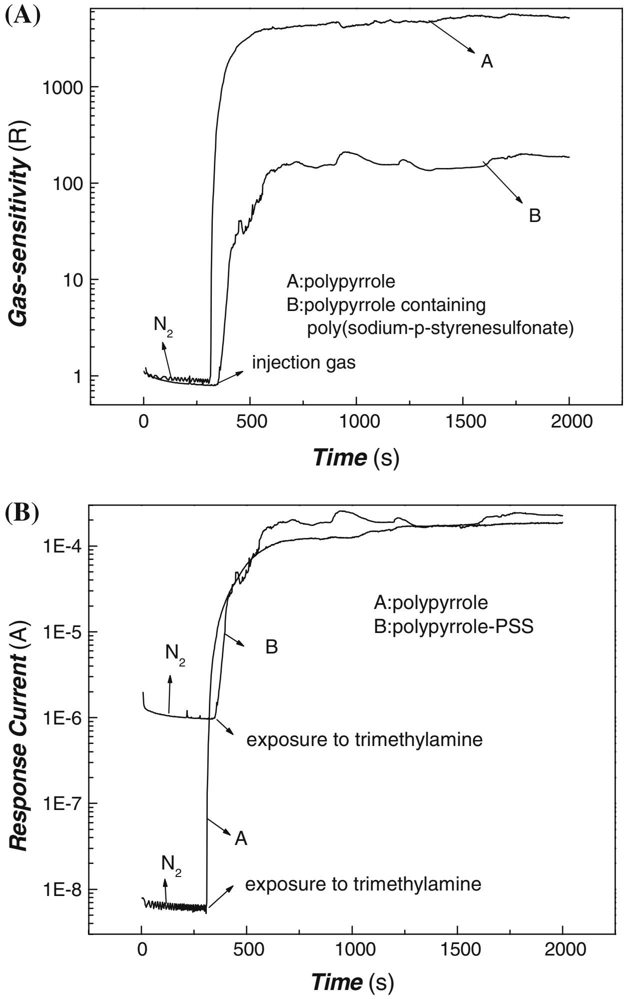


Fig. 6 Effects of poly (sodium-p-styrenesulfonate) on the gas-sensitivity of polypyrrole film

poly (sodium-p-styrenesulfonate), the value of sensitivity was still up to 2 orders, it has been enough for application design of sensor. The main reason that the gas-sensitivity decreased is the results of the baseline current of sensor enhanced by adding a small amount of poly (sodium-p-styrenesulfonate) (see Fig. 6B). Figure 6B shows that, comparing to that polypyrrole film, the conductivity of the resulting product PPy/Poly(sodium-p-styrene sulfonat) film is much higher, is has increased about 2 orders. This illustrated that the effects of poly(sodium-p-styrene sulfonat) on the conductivity of polypyrrole film was remarkably, the baseline current of sensor was increased greatly. This is favorable to determine the signal of sensor. It may adjust the ranges of determination, and be favorable to the stability of determination.

The cycle reproducibility of film sensor

The results of cycle reproducibility of film sensor were shown in Fig. 7.

Figure 7 shows that this film in our experiment has good repeatability and stability.

Effects of moisture on the sensitivity of composite film sensor

It is well known that the effects of moisture on the sensitivity of polyrrole film sensor are greatly. Consequently, to improve the resistance in moisture of sensor is very important for applications. The effects of a small amount of poly (sodium-p-styrenesulfonate) on the resistance in moisture of polypyrrole film are shown in Fig. 8.

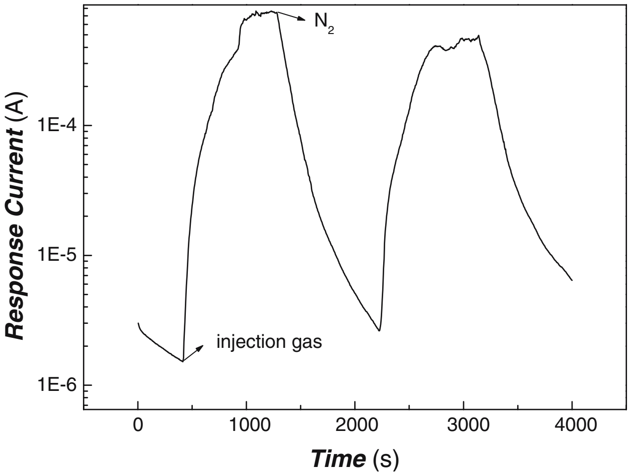


Fig. 7 Cycle test examination of the resulting product PPy/Poly(sodium-p-styrene sulfonat) to trimethylamine (3.189×10^{-1} mol/m^3)

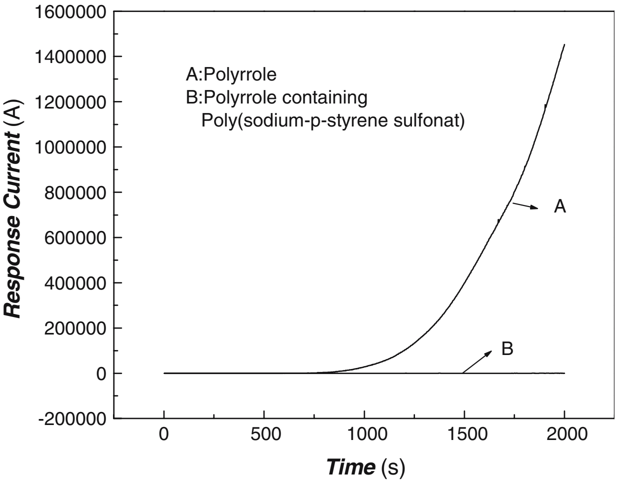


Fig. 8 Effects of moisture on the sensitivity of composite film sensor

Figure 8 shows that the resistance in moisture of sensor is improved obviously by a small amount of poly (sodium-p-styrenesulfonate) added.

Conclusion

In summary, water-soluble polypyrrole was obtained via oxidative polymerization approach in the presence of a small amount of poly (sodium-p-styrenesulfonate). The film-forming technology was improved greatly, and the resistance in moisture of sensor was also improved obviously by a small amount of poly (sodium-p-styrenesulfonate) added. Although the gas-sensitivity value was decreased at certain extent, this film still shows good gas-sensitivity and rapid response to trimethylamine of 3.189×10^{-1} mol/m^3, easily recovered with N_2 at room temperature, good selectivity to analogy and interferent gases, and has good perspective for application in sensor and electronic nose.

This method is very simple and feasible, is also prone to produce it at large scale, and has low cost, no environmental pollution. It will be possible to be used in other device fields.

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