Synthesis and Humidity Sensitive Properties of Pyrrole-Based Polyelectrolytes

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ABSTRACT: Pyrrole (Py)-based polyelectrolytes (Py-PE): P(Py-COOLi), P(Py-COONa), and P(Py-COOK) was synthesized, characterized, and used to prepare thin film resistive humidity sensors. Their humidity sensitive properties have been investigated, and sensing mechanism was presented. The Py-PE contains PPy as backbone and the side chain bearing carboxylic salt group, which made its sensor exhibited a very wide humidity sensing range of 0–97% relative humidity (RH), high conductivity even at very low humidity, and both ionic and electronic conduction contributed to its conductivity. Among all the Py-PE, P(Py-COOK) showed high sensitivity, with the impedance changing of about three orders of magnitude (10^3–10^6 Ω) from 97 to 0% RH, whereas P(Py-COONa) showed quick response for both absorption (12.5 s) and desorption (15.2 s). Py-PE prepared is promising for preparation of thin film resistive humidity sensors capable of detecting low humidity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1287–1293, 2009

Key words: pyrrole; polyelectrolyte; humidity sensitivity; humidity sensor

INTRODUCTION

It is well known that conductive polymers have been intensively investigated in the applications including chemical and biosensors, actuators, photovoltaics, rechargeable batteries, separation films, etc.[1] As one of the most important conductive polymers, Polypyrrole (PPy) received much attention because of its easy of preparation, high conductivity, good environmental stability, and nontoxicity. PPy was used as electromagnetic interference shielding (EMI) materials, biosensors, electrodes for solid-state batteries, and solid-state capacitors, etc.[2–5]

In recent years, some attentions have been attracted to the humidity sensing properties of PPy and its composites. Geng[6] reported that the humidity sensing properties of PPy could be improved greatly by extending the polymerization time. Tandon and Suri[7] synthesized iron oxide-polypyrrole nanocomposites, and found that the PPy concentration has great influence on the humidity sensitivity. Cho[8] studied the sensing behaviors of PPy sensor under low humidity condition. Su and Huang[9] prepared TiO_2 nanoparticles/PPy composite and investigated its humidity sensitive properties. However, the sensors based on PPy exhibited either high resistance or low sensitivity under low humidity, which result in great difficulties for sensors to measure or distinguish the electrical response to humidity change.

Polymer electrolytes have been widely used in the preparation of resistive-type humidity sensors in the past few years.[10–19] Although they exhibit many advantages: ease of preparation, low cost, quick response, and high sensitivity, etc., the detection of low humidity remains to be a problem, because their extremely low conductivity under very dry atmosphere brought about great difficulties for measurement.

In this article, a novel pyrrole-based polyelectrolytes (Py-PE) was synthesized for the construction of the thin film resistive humidity sensors. Their humidity sensitive properties have been investigated and sensing mechanism was presented. This study in turn is a development based upon our previous work on resistive-type polymeric humidity sensors based on doped conjugated polymer and polyelectrolytes, etc.[12,14,16–24]

EXPERIMENTAL

Materials

All the reagents used in this study were of analytical grade. Pyrrole (Py) was distilled before use. *p*-

Toluenesulfonyl chloride was purified by recrystallization from benzene/petroleum ether (1/20, v/v). Anhydrous tetrahydrofuran (THF) was obtained by distillation over sodium/diphenyl ketone. Anhydrous 1,2-dichloroethane was obtained by distillation over calcium chloride anhydrous. Succinic anhydride was purified by recrystallization from ethanol. All the other chemicals were purchased from domestic chemical markets and used as received.

Measurements

FTIR spectra were recorded on a Bruker Vector 22 IR spectrometer. ^{1}H NMR measurements were carried out on Advance DMX500, 500 MHz spectrometer (solvent: CDCl$_3$; internal standard: tetramethylsiliane). UV–vis spectra were recored on a Varian Cary 100 Bio UV–vis spectrophotometer. The morphologies of the sensitive films were observed by scanning electron microscopy (SEM) instrument (Sirion FEI Company). The impedance response of the humidity sensor to relative humidity (RH) and the hysteresis were measured by using an in-house built electric circuit at 1 V and 1 KHz. Different humidities were obtained by controlling the ratio of dry and wet air. The response time was determined over different saturated salt solutions in their equilibrium (MgCl$_2$ for 33% RH and K$_2$SO4 for 97% RH). The time to reach 90% of the impedance change was denoted as the response time (t90%). In this article, every impedance parameter was tested at least three times, and the result deviations were less than 1%. All the measurements were carried out at room temperature.

Synthesis of 1-(toluene-4-sulfonyl)-1H-pyrrole (1)

A mixture of Py (24.8 g, 0.37 mol), crushed potassium hydroxide (42.1 g, 0.75 mol), and THF (300 mL) was stirred and cooled to 0°C, then a soliution of *p*-Toluenesulfonyl chloride (77.6 g, 0.41 mol) in THF (60 mL) was added dropwise over a period of 2 h. The mixture was stirred for another 2 h at 0°C, and then run overnight at room temperature. After reaction was quenched with diethyl ether (500 mL), the resulting solution was washed with copious amounts of deionic water (5 × 250 mL), then the organic layer was separated, and the solvent was removed by rotary evaporation. The residue was recrystallized from methanol (200 mL) to yield the white crystalline solid (1). FTIR (KBr pellet, cm^{-1}): 3143, 1458, 1361, 1182, 1171, 1091, 1059, and 1034. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 2.39 (3H, s, CH$_3$), 6.28 (2H, t, Py), 7.16 (2H, t, Py), 7.28 (2H, d, tosyl), 7.76 (2H, d, tosyl).

### Synthesis 4-oxo-4-[1-(toluene-4-sulfonyl)-1H-pyrrol-3-yl]-butyric acid (2)

To a suspension of aluminum chloride anhydrous (15 g, 0.11 mol) in 200 mL of 1,2-dichloroethane, succinic anhydride (5.5 g, 0.51 mol) was added at 25°C. After the solid was dissolved, a solution of 1 (11.1 g, 0.05 mol) in 60 mL of 1,2-dichloroethane was added dropwise, and the mixture was stirred at 25°C for 2 h. Then the reaction was quenched with ice water (500 mL) and the crude product was extracted with dichloromethane. The organic layer was washed with water and dried over anhydroussodium sulfate. After the solvent was removed by rotary evaporation, the residue was recrystallized to give a white crystalline solid (2). FTIR (KBr pellet, cm^{-1}): 3500–2500, 1712, 1676, 1375, 1173, 1103, and 1066. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 2.42 (3H, s, CH$_3$), 2.73 (2H, t, CH$_2$), 3.07 (2H, t, CH$_2$), 6.68 (1H, dd, Py), 7.13 (1H, dd, Py), 7.26 (1H, s, Py), 7.34 (2H, d, tosyl), 7.75–7.82 (2H, m, tosyl).

Synthesis 4-[1-(toluene-4-sulfonyl)-1H-pyrrol-3-yl]-butyric acid (3)

A mixture of zinc metal (45.8 g) and mercuric chloride (4.58 g) in 60 mL of water and 3 mL of 12*M* HCl was stirred at room temperature for 20 min, and then the solvent was removed. To the solid were added 28 mL of water, 66 mL 12*M* hydrochloric acid, 300 mL of toluene, and 2 (18.64 g, 0.058 mol). The mixture was refluxed at 100°C for 16 h, and then cooled. The organic fraction was extracted with toluene, then washed with water, and dried over anhydrous sodium sulfate. After the solvent was removed by rotary evaporation, the residue was recrystallized from toluene to give white crystals (3). FTIR (KBr pellet, cm^{-1}): 3500–2500, 1707, 1367, 1171, 1102, and 1061. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 1.76 (2H, quintet, CH$_2$), 2.19–2.39 (7H, m), 6.05 (1H, dd, Py), 6.82 (1H, m, Py), 6.98 (1H, dd, Py), 7.16–7.21 (2H, m, tosyl), 7.60–7.65 (2H, m, tosyl).

Synthesis 4-(1H-Pyrrol-3-yl) butyric acid (4)

A mixture of 3 (8 g, 13.2 mmol), 60 mL of sodium hydroxide aqueous solutioin (5*M*), and 60 mL of methanol was refluxed at 80°C for 2.5 h, and then methanol was removed by rotary evaporation. The residue was diluted with ice water, the pH of which was adjusted to two with hydrochloric acid (6*M*) at 0°C, and then extracted with ethyl acetate. The extracts were dried over anhydrous sodium sulfate, solvent was removed by rotary evaporation, and the residue was recrystallized from toluene/hexane (1:1, v/v) to give white crystals (4). FTIR (KBr pellet, cm^{-1}): 3500–2500, 3340, 1701, 1284, 1229, 1192, and 1064. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 1.93 (2H,
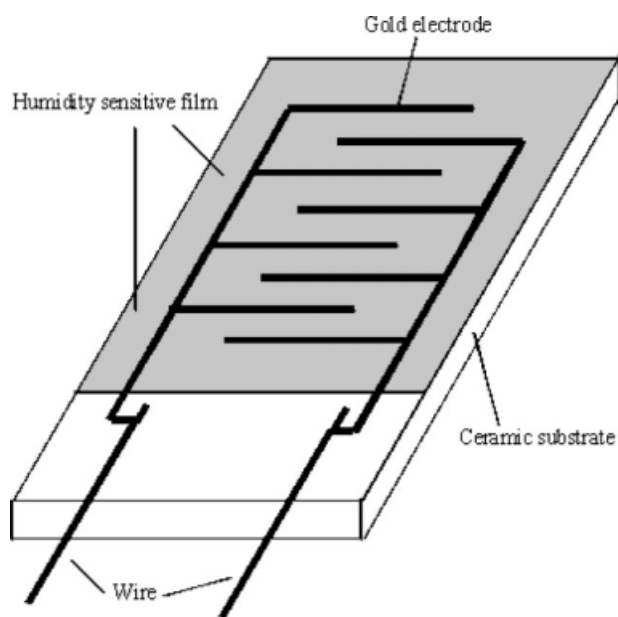
Scheme 1 Structure illustration of interdigitated gold electrode.

quintet, CH_2), 2.40 (2H, t, CH_2), 2.57 (2H, t, CH_2), 6.08 (1H, m, NH), 6.56–6.60 (1H, m, Py), 6.69–6.73 (1H, m, Py), 7.25–7.29 (1H, m, Py).

Fabrication of humidity sensors

One gram of 4-(1H-Pyrrol-3-yl) butyric acid (Py-COOH) was dissolved in 10-mL absolute ethanol, and dipcoated on a clean interdigitated gold electrode (Scheme 1) with a ceramic substrate (12 mm × 5 mm × 0.5 mm).

After dried at room temperature, the as-coated electrode was dipped into the aqueous solution of $FeCl_3$ and p-toluenesulfonic acid (TSA) for 5 min. Afterwards, it was washed with absolute ethanol for three times to remove excessive $FeCl_3$, TSA, and unreacted 4-(1H-pyrrole-3-yl) butyric acid. Subsequently, the as-prepared electrode was dipped into the $0.01M$ aqueous alkali (LiOH, NaOH, and KOH) for 1 min, then washed with deionic water for three times, and dried by heating at 80°C for 0.5 h to afford a polymer thin film resistive-type humidity sensor. The thickness of the polymer film is 2–3 μm.

RESULTS AND DISCUSSION

Synthesis and characterization

Py-based polyelectrolytes, named Py-PE was synthesized by two processes. Firstly, a Py derivative, 4-(1H-pyrrole-3-yl) butyric acid (Py-COOH), was prepared by Friedel-Crafts reaction, as shown in Scheme 2. Initially, Py was protected with a tosyl group, and then Friedel-Crafts acylation of the tosyl-protected Py using succinic anhydride and $AlCl_3$.

Transformation of the ketone group was achieved by Clemmensen reduction and then the phenylsulfonyl protecting group was readily removed by subsequent alkaline hydrolysis to yield desired Py-COOH. Py-COOH is a type of 3-alkylpyrrole, which bearing a terminal carboxyl group. Because it is a C-3 or C-4 position substituted Py, its C-2 and C-5 positions still remained polymeric activity.[25,26]

Secondly, Py-PE: P(Py-COOLi), P(Py-COONa), and P(Py-COOK) was synthesized by simultaneous polymerization and formation of Py-COOH polymer film (named P(Py-COOH), Py-PE precursor) on the interdigitated gold electrode and then reacted with the aqueous alkali (LiOH, NaOH, KOH), as shown in Scheme 3. The Py-PE so prepared contains PPy as backbone and the side chain bearing carboxylic salt group.

Figure 1 shows the UV–vis spectra of PPy, Py-PE: P(Py-COOLi), P(Py-COONa), P(Py-COOK), and its precursor P(Py-COOH) in films. As shown in the absorption spectra, the maximum absorption wavelengths of the PPy, P(Py-COOLi), P(Py-COONa), and P(Py-COOK) are at around 460, 400, 395, and 385 nm, respectively, which are attributed to the π-π* transition of π-conjugated main chain. When compared with the PPy, Py-PE shows blue shift, which could be owing to decreased conjugated length of the PPy backbone.[27] Furthermore, the blue shift becomes obvious with increasing the radius of substituted cation (Li^+, Na^+, K^+) of Py-PE. However, for the precursor P(Py-COOH), no obvious absorption peak is observed in the UV–vis spectra (Fig. 1), which perhaps due to the influence of hydrogen
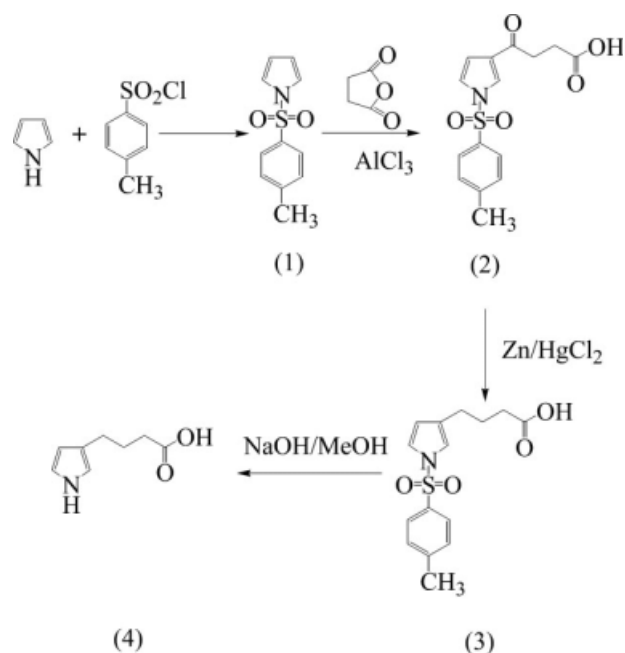

Scheme 2 Synthesis route of 4-(1H-Pyrrol-3-yl) butyric acid (Py-COOH).

bonds of P(Py-COOH). The above results indicated that the synthesis routes (Schemes 1 and 2) are successful, and Py-PE was obtained. Py-PE is a novel humidity sensitive material, having both ionic and electronic conductivity.

To have a better understanding of humidity sensitive behavior of Py-PE, the morphologies of the films were examined. Figure 2 shows the SEM micrographs of PPy, Py-COOH, P(Py-COOH), P(Py-COOLi), P(Py-COONa), and P(Py-COOK). It can be seen that the micrograph of PPy [Fig. 2(A)] is congregated particles. Its average size is about 300 nm. The monomer of Py-COOH [Fig. 2(B)] is well dispersed on the surface of electrode with branch shape, whereas after polymerized, the P(Py-COOH) forms PPy like particles [Fig. 2(C)]. However, the morphologies of P(Py-COOLi), P(Py-COONa), and P(Py-COOK) are quite smooth and uniform films and no any folds or cracks on it [Fig. 2(D–F)]. These results indicated that after P(Py-COOH) reacted with aqueous alkali, Py-PE formed has better film-formability for the preparation of thin film humidity sensors.

Humidity sensitive properties

Thin film resistive humidity sensors based on Py-PE were prepared by the following procedure: dip-coating the solution of Py-COOH in absolute ethanol on the interdigitated gold electrodes, then simultane-
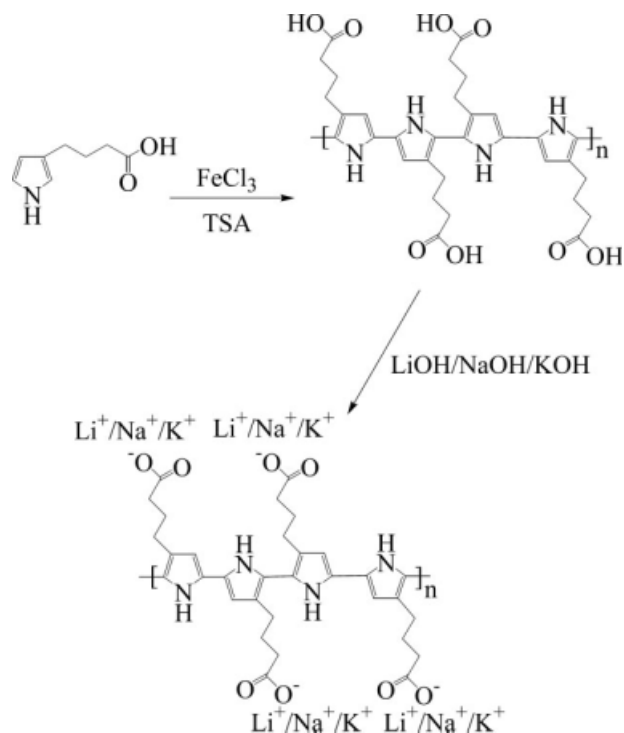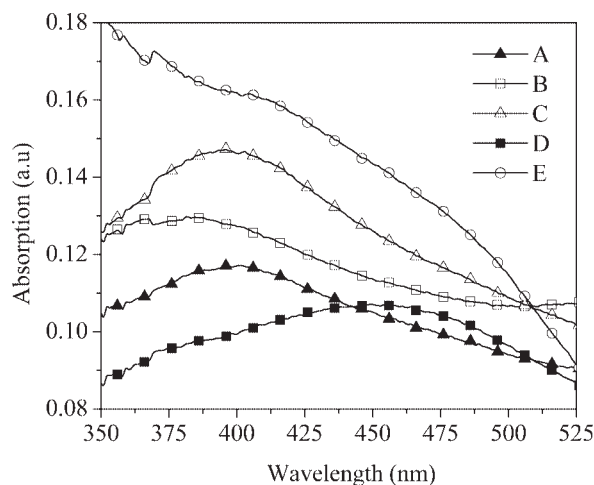

Figure 1 UV–vis spectra of P(Py-COOLi) (A); P(Py-COOK) (B); P(Py-COONa) (C); PPy (D); and P(Py-COOH) (E) in films on quartz glass.

ously polymerizing and forming of P(Py-COOH) films and reacting with aqueous solution of alkali. Their humidity sensitive properties are illustrated in Figure 3. As shown in the figure, the sensor based on P(Py-COOH) exhibits a low sensitivity over a wide range of humidity (0–97% RH), with little impedance changing on a semilogarithmic scale. While the sensors based on Py-PE (P(Py-COOLi), P(Py-COONa), P(Py-COOK)) exhibit a high sensitivity with the impedance changing of 1–3 orders of magnitude at same conditions. Especially, the impedance of the P(Py-COOK)-based sensor changes about three orders of magnitude (10^3–10^6 Ω) from 97 to 0% RH, showing much high sensitivity. The results indicated that the humidity sensitive performance of the sensors could be improved by bearing carboxylic salt group in the pendant group of PPy, and arised with increasing the radius of the substituted cation (Li^+, Na^+, K^+) in the carboxylic salt group. It is probably because K^+ possesses less activation energy.[28,29] It is quite worth noting that the impedance of Py-PE is still less than 10^7 Ω at dry atmosphere ($\sim$ 0% RH), which is not often seen for resistive polymeric humidity sensitive materials. Thus Py-PE materials can be used for preparing resistive-type humidity sensors capable of detecting very low humidity.

Figure 4 shows the impedance response of the sensors during the desorption and absorption process and the sensors exhibit the hysteresis of 2.4, 4.7, and 4.3% RH for P(Py-COOLi), P(Py-COONa), and P(Py-COOK), respectively. The response time of the sensors was also investigated. It is another important parameter for evaluating the performance of humidity sensors, which is defined as the time for the electrical response of a sensor to reach 90% of its steady state values. The typical response time of a humidity
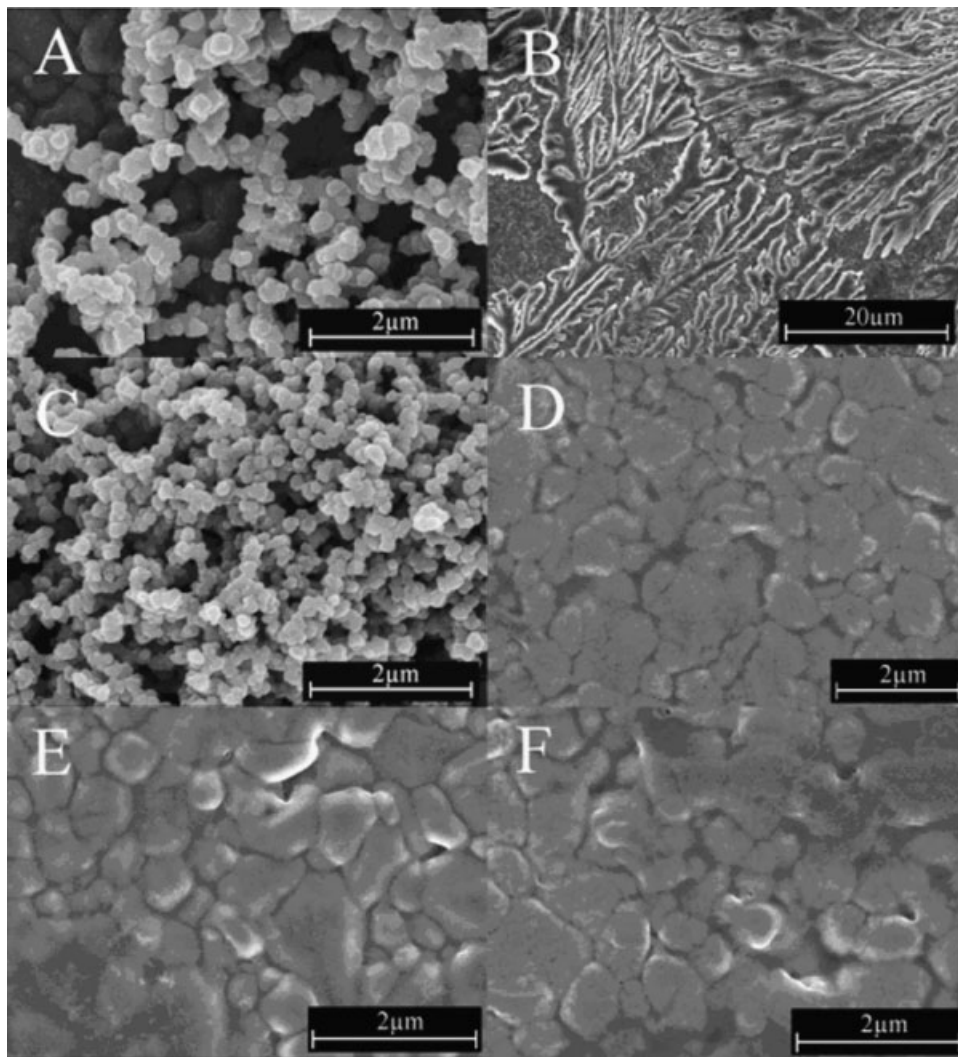

Scheme 3 Synthesis route of Py-PE humidity sensitive materials.

Figure 2 SEM micrographs of (A) PPy; (B) (Py-COOH); (C) P(Py-COOH); (D) P(Py-COOLi); (E) P(Py-COONa); and (F) P(Py-COOK).
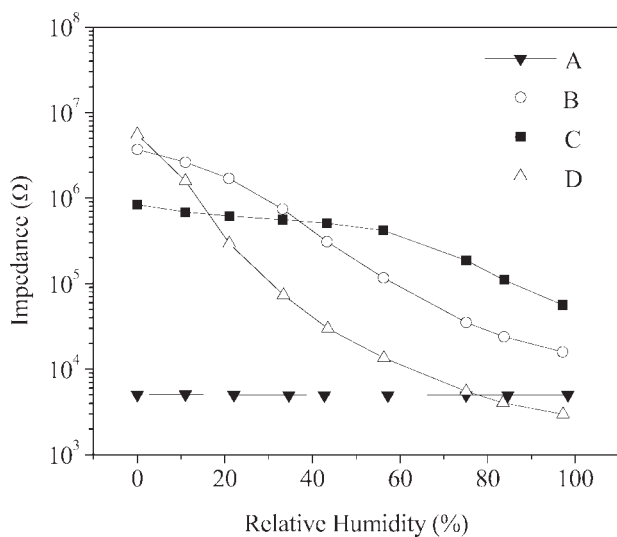

Figure 3 Impedance as a function of humidity for sensors based on the Py-PE precursor P(Py-COOH) (A) and Py-PE: P(Py-COONa) (B); P(Py-COOLi) (C); P(Py-COOK) (D).
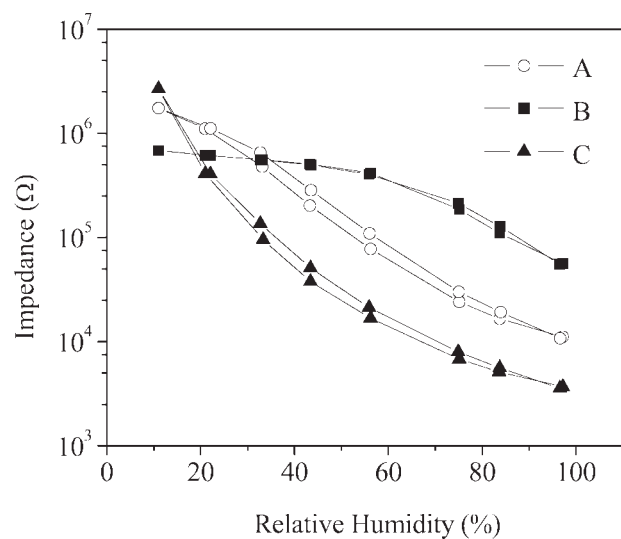
Figure 4 Hysteresis of sensors based on the Py-PE: P(Py-COONa) (A); P(Py-COOLi) (B); P(Py-COOK) (C).
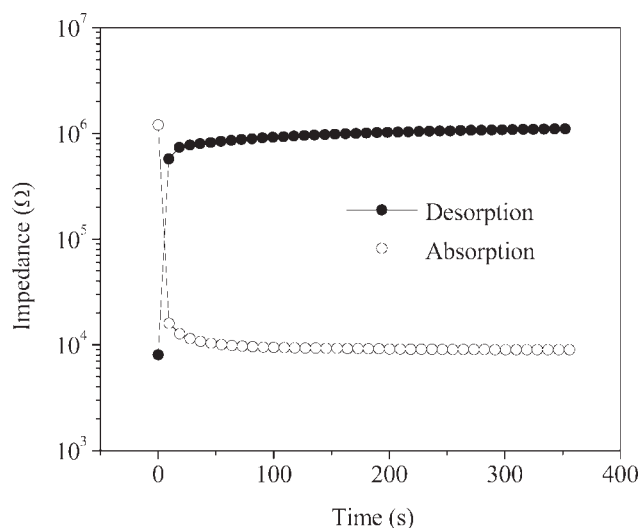
Figure 5 Response time of P(Py-COONa): desorption (A) and absorption (B).

sensor based on P(Py-COONa) is shown in Figure 5. It can be seen that P(Py-COONa)-based sensor exhibits a fast response to the humidity change, and the response time was calculated to be 12.5 s and 15.2 s for absorption and desorption process, respectively. P(Py-COOLi)-based sensor exhibits a slow absorption (36.1 s) and a fast desorption (7.7 s). In contrast, P(Py-COOK) shows a fast absorption (11.7 s) and a slow desorption (78.8 s). This is because the different substituted captions in the pendant group of PPy made the polymer sensitive films have different degrees of interaction with water molecules. In general, the stronger interaction leads to the faster absorption of water molecules and the slower desorption. For PPy with ─COOK, the interaction between water molecules and the polymer sensitive film is the strongest due to its shorter conjugation length and better hydrophilic,[28,29] in contrast, the PPy with -COOLi shows the weakest interaction and PPy with ─COONa shows the moderate interaction. Thus it can be seen from the above results that the moderate interaction between water molecules and polmer sensitive film is the best for the sensor to have very quick response in both adsorption and desorption process.

Humidity sensing mechanism

For the polyelectrolyte-based humidity sensors, the conduction mechanism is mainly ionic, and sensing behavior is strongly dependent on both the kind and concentration of ions and the water absorption ability of the sensing film.[12,23,24,30,31] Thus the polyelectrolyte-based humidity sensors usually have difficulty in detecting low humidity due to the high impedance involved. Although it is known that PPy is a typical intrinsic conducting polymer, its conduc-

tion mechanism is mainly electronic. Moreover, PPy possesses high conductivity even at very dry atmosphere ($\sim$ 0% RH), but exhibits very low sensitivity to moisture due to weak interaction between conjugated main chain and water molecules. In this study, Py-based polyelectrolytes (Py-PE) prepared composed of conjugated polymer PPy as backbone and the side chain bearing carboxylic salt group. Thus, the sensor based on Py-PE exhibits both ionic and electronic conduction contributed to its conductivity, but it is different for both to play dominant role over the range of tested humidity. At a low humidity, even at dry atmosphere ($\sim$ 0% RH), the electronic conduction may play a dominant role because of the insufficient dissociation of carboxylic salt groups in Py-PE for providing enough free carrier ions, which is supported by the fact that the impedance of Py-PE is still less than 10^7 Ω at dry atmosphere (Fig. 3). In contrast, with the humidity increases, the ionic conduction may become more important and stepwise dominant due to the absorbed water molecules facilitate the dissociation of ion-pairs of the carboxylic salt group, resulting in Py-PE possesss low impedance and high sensitivity. Therefore, Py-PE material is promising for preparation of thin film resistive humidity sensors capable of detecting low humidity and having high sensitivity.

CONCLUSIONS

A novel thin film resisitive humidity sensor based on Py-PE (P(Py-COOLi, P(Py-COONa), P(Py-COOK)) can be prepared by simultaneous polymerization and formation of Py-PE precursor (P(Py-COOH)) film on the interdigitated gold electrode and then reaction with the aqueous alkali (LiOH, NaOH, KOH). The sensor exhibits a very wide humidity sensing range of 0–97% RH, high conductivity even at very low humidity, and both ionic and electronic conduction contributed to its conductivity. The humidity sensing behavior of the Py-PE depends on its chemical structure containing PPy as backbone and the side chain bearing carboxylic salt group. Py-PE-based sensors are capable of detecting low humidity.

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