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Humidity sensor based on a cross-linked porous polymer with unexpectedly good properties

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A humidity sensitive polymer was synthesized based on the derivative of triphenylphosphine by Friedel– Crafts alkylation. The polymer was formed of a hydrophobic skeleton with hydrophilic ions modified on phosphorous atoms evenly. The resultant polymer shows nanoporous characteristics. A humidity sensor based on the amphiphilic porous polymer shows unexpectedly good sensing properties, including high sensitivity, small humidity hysteresis, rapid response and recovery, and good stability. The good stability of the sensor is attributed to the cross-linked skeleton structure of the polymer, even though the content of ions in the polymer is high. These results demonstrate that porous polymers modified with certain hydrophilic groups are promising materials for high performance humidity sensors.

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1. Introduction

Humidity sensors based on different kinds of materials, such as ceramics,^{1,2} organic polymers³⁻⁵ and organic-inorganic composites⁶⁻⁸ have been reported in recent years. Among these humidity sensitive materials, organic polymers are very attractive because of their advantages of solution-processable applications and low cost. Polymeric humidity sensors with high sensitivity and rapid response properties have been developed.^{5,6} Nowadays, the main challenge of polymeric humidity sensors is their stability under high humidities. Since most of the humidity sensitive polymers are amphiphilic, the polar groups (-COOH, -NR₃⁺Cl⁻, -SO₃H etc.) in the polymers could interact strongly with water molecules and may result in the dissolution of polymers at high humidities, which would decrease the measurement accuracies and stabilities of the sensors. An effective method to improve the stability of polymeric humidity sensors at high humidities was realized by forming cross-linked films after coating the sensitive materials on the surface of electrodes.^{3,9,10} However, it is difficult to control the structure of the resultant polymers and to obtain sensors with good reproducibility, since these crosslinking reactions usually occur in solid state.

Porous organic polymers have attracted the attention of many researchers in past few years,¹¹⁻¹⁵ which have been used in many different application fields, such as gas storage,^{16,17} catalyst,¹⁸ and light harvesting¹⁹ *etc.* Thanks to their good stability and porosity, "amphiphilic" porous polymers formed from crosslinking reaction may be a good choice as humidity sensitive materials. The cross-linked skeleton could afford good structural stability while the porosity characteristic is beneficial for the transport of water molecules in polymers. In our previous work, a hydrophobic porous polymer was used as host to load humidity sensitive LiCl for preparing humidity sensitive composites.²⁰ Herein, a novel humidity sensitive amphiphilic porous polymer was synthesized by Friedel–Crafts alkylation. The obtained polymer could be used for humidity sensors directly without loading humidity sensitive materials. Humidity sensor based on this "single" polymer showed unexpectedly good sensing properties.

2. Experimental

2.1 Synthesis of materials

(1) Synthesis of monomer TPPBr. Triphenylphosphine (2.41 g, 9.20 mmol) and 1-bromohexane (1.51 g, 9.20 mmol) were added to the flask and the mixture was heated to 80 °C for 15 h. Then petroleum ether (100 mL) was added to the above mixture, and the resultant solid was filtered and washed with plenty of petroleum ether to afford a white solid product (2.54 g). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.92–7.87 (m, 6H), 7.83–7.80 (m, 3H), 7.74–7.71 (m, 6H), 1.67–1.63 (m, 4H), 1.26–1.25 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 2H).

(2) Synthesis of polymer PTPPBr. Polymer PTPPBr was synthesized by Friedel–Crafts alkylation according to the reported route^{21,22} with higher reaction temperature. Monomer TPPBr (1.50 g, 3.52 mmol), anhydrous 1,2-dichloroethane (7 mL), formaldehyde dimethyl acetal (1.25 mL, 14.08 mmol) and iron(m) chloride (2.26 g, 14.05 mmol) were added to the flask, and the mixture was degassed and heated to 100 °C for 24 h. After cooling down to room temperature, the obtained solid was filtered, and washed with plenty of methanol till the filtrate was clear. Then the resultant dark red solid was further purified by soxhlet extraction with methanol for 24 h and dried under vacuum at 40 °C for 12 h.

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2.2 Sensor preparation

The polymer was mixed with *n*-butanol to form a paste, then the paste was coated on a ceramic substrate (6 mm \times 3 mm, 0.5 mm thick) with five pairs of Ag–Pd interdigitated electrodes (electrodes width: 0.15 mm; electrodes distance: 0.15 mm) to form a sensing film dried in air at room temperature for 12 h. Finally, the humidity sensors were obtained after aging at the relative humidity (RH) of 95% with the alternating current (AC) of 1 V, 100 Hz for 24 h to improve their stability and durability.

2.3 Measurements

The morphology of PTPPBr sample was performed on a JEOL JSM-6700F scanning electron microscopy (SEM). The microstructure of the film was checked using a JEM-2100F transmission electron microscopy (TEM), with an accelerating voltage of 200 kV. Nitrogen (N2) isotherms were obtained at 77 K on a Micromeritics Tri-star 3000 analyzer. Samples were pretreated by degassing for 12 h at 150 °C. The IR spectrum of PTPPBr was obtained on a WQF-510A FT-IR spectrometer. Thermal gravimetric analysis (TGA) was undertaken on a Perkin-Elmer thermal analysis system at a heating rate of 10 °C min⁻¹ and a nitrogen flow rate of 80 mL min⁻¹. The humidity sensitive properties were investigated by recording the electrical response of the sensor at 1 V AC under different RH by a ZL-5 intelligent LCR analyzer at \sim 20 °C. The RH atmospheres were produced by different saturated salt solutions in their equilibrium states, including LiCl for 11% RH, MgCl₂ for 33% RH, Mg(NO₃)₂ for 54% RH, NaCl for 75% RH, KCl for 85% RH, and KNO₃ for 95% RH. The uncertainty of the RH values is $\sim \pm 1\%$.

3. Results and discussions

3.1 Synthesis and characterization of polymer PTPPBr

The synthetic routes to polymer PTPPBr are shown in Scheme 1. Triphenylphosphine was selected as the raw material because it is beneficial for constructing porous polymer skeleton with three phenyl rings in each molecule, and its quaternary phosphorus salt (TPPBr) could be prepared to provide hydrophilic property for the polymer. TPPBr was then used for Friedel-



Scheme 1 The synthetic route to polymer PTPPBr.

Crafts alkylation directly with formaldehyde dimethyl acetal as the crosslinker. Since the strong electrophilic substitution reactivity of TPPBr, stable polymer framework with hydrophilic groups could be obtained.

The structure of PTPPBr was determined by IR spectra, as shown in Fig. 1a. The strong absorptions at 669, 689, 867 cm^{-1} and absorptions between 1005 and 1121 cm⁻¹ are assigned to the stretching of C-H in the phenyl rings. The absorption at 1365 cm⁻¹ comes from the stretching of alkyl groups. The absorptions at 1430 and 1489 cm^{-1} come from the aromatic C= C stretching. And the stretching of P-C=C (p- π conjugation) shows a strong vibration peak at 1647 cm⁻¹. The IR results demonstrate that the desired polymer has been obtained. The thermal property of PTPPBr was investigated by TGA with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. As shown in Fig. 1b, the onset of the thermal decomposition of PTPPBr is 183 °C with a 5% weight lost. The good thermal property is beneficial for the stability of the humidity sensors, because the working temperature of humidity sensors is usually lower than 100 °C.

To investigate the permanent porosity of PTPPBr, N2 sorption isotherms were measured at 77 K and the results are shown in Fig. 2a. The adsorption isotherm displays a N2 uptake at low relative pressure $(P/P_0 < 0.01)$ demonstrating the existence of microporous structure. PTPPBr also exhibits N2 sorption isotherms with an upward deviation in the relative pressure range of 0.20-0.99. The microporous volume and total volume calculated with N₂ adsorption at $P/P_0 = 0.99$ is 0.03 and 0.13 cm³ g^{-1} , respectively. The Brunauer–Emmett–Teller (BET) surface area of the polymer is 72 m² g⁻¹ from N₂ physisorption. PTPPBr shows a wide pore size distribution with the pore diameter centering around 1.1 and 5.0 nm (Fig. 2b). SEM and TEM images of PTPPBr sample are shown in Fig. 2c and d, respectively. As can be seen in Fig. 2c, the polymer stacks with network aggregates, and unregular nanopores form in the sample as shown in the inset of Fig. 2c, which are beneficial for the adsorption and transport of water molecules in the polymer. The TEM image (Fig. 2d) also confirms the porous amorphous structure of PTPPBr. Therefore, the polymer could provide channels for transport of water molecules. And since the framework is formed of organic cross-linked groups, it is beneficial for the stability of the polymer at high humidities.

3.2 Humidity sensing properties of PTPPBr sensor

Operating frequency is an important parameter for resistancetype humidity sensor. To determine the optimal working parameters, the impedances of PTPPBr sensor under different RH atmospheres at different frequencies (20, 100, 1 k, 10 k and 100 kHz) at \sim 20 °C were measured and the results are shown in Fig. 3. The impedance of the sensor under certain RH decreased with increasing working frequency. And it is worthy to note that the impedance differences at low RH are much bigger than that at high RH. The sensing curves almost overlapped at RH higher than 80%, indicating the effect of frequencies on impedance was very little in this range. On the other hand, the impedances decreased with the increasing RH, due to the increasing water



Fig. 1 (a) The IR spectrum of polymer PTPPBr; (b) TGA curve of PTPPBr with a heating rate of 10 $^{\circ}$ C min⁻¹ in N₂



Fig. 2 (a) N₂ adsorption/desorption isotherms measured at 77 K and (b) the width distribution profile of PTPPBr; (c) SEM and (d) TEM images of PTPPBr.



Fig. 3 Impedances of PTPPBr sensor at different RH under different frequencies (1 V AC).

molecules adsorbed onto the sensitive layer with RH. The sensing curve at 100 Hz exhibits the best linearity, and under this frequency the sensor is very sensitive in whole humidity range with the impedance changing four orders of magnitude from 11% to 95% RH. So the optimum measurement condition was fixed at AC 1 V, 100 Hz in the following experiments.

Fig. 4 shows the humidity hysteresis characteristic of PTPPBr sensor under AC 1 V, 100 Hz. The impedance of the sensor was first measured from low to high RH (11% to 95% RH, the adsorption process), and then in the opposite direction (95% to 11% RH, the desorption process). The PTPPBr sensor shows very little humidity hysteresis in the adsorption and desorption processes at whole RH range, with a maximum humidity hysteresis of 2% RH under ~75% RH. The humidity hysteresis of PTPPBr sensor is much lower than that based on amphiphilic polymers.^{23,24} The high sensitivity and good humidity hysteresis property of the sensor are attributed to the porous structure of the sensitive material. On the one hand, it is sensitive to the humidity even at low humidity range below 33% RH, because of



Fig. 4 Humidity hysteresis of PTPPBr sensor (1 V AC, 100 Hz).

the large quantity of hydrophilic quaternary phosphorus groups in the polymer, which could interact with water molecules. On the other hand, quaternary phosphorus salt groups are modified separately on the cross-linked polymer framework, and these hydrophilic groups would not aggregate even at high RH, so the sensitive layer is not "saturated" even at 95% RH, and the humidity hysteresis is really small.

Impedance curve of PTPPBr at four continuous water adsorption and desorption processes between 11% and 95% RH is shown in Fig. 5 (since the sensor has to be exposed to the laboratory atmosphere in the process of humidity change, the switching process between 11% and 95% RH was accomplished as quickly as possible, which could be done less than 1 s). The time taken by a sensor to achieve 90% of the total impedance change is defined as the response or recovery time.²⁵ For PTPPBr sensor, the response time was 3 s when RH was changed from 11% to 95%, and the recovery time was 40 s in the opposite process. These values are comparable with the sensors based on hydrophilic polymers.^{10,23} The response and recovery properties are consistent with the little humidity hysteresis of the sensor. The rapid response speed is also attributed to the large quantity of hydrophilic quaternary phosphorus groups in the polymer, which could interact quickly with water molecules and the rapid recovery speed is contributed to the separation of sensitive points in the framework and the porosity characteristic property of polymer PTPPBr.

3.3 Sensing mechanism of PTPPBr sensor

Complex impedance plots are usually used to study the humidity sensing mechanism of materials.26,27 The complex impedance spectra of PTPPBr sensor shown in Fig. 6 were measured at 1 V with the operation frequency changed from 20 Hz to 100 kHz under different humidities. The complex impedance and complex angle at different conditions were measured and the real part and the imaginary part of the complex impedance were obtained and magnified on the same plane. At 11% and 33% RH, the curve is a part of a semicircle, which could be described by an equivalent circuit comprising a resister and a capacitor connected in parallel, and a semicircle reveals the existence of H⁺ hopping conduction.^{28,29} As the RH increased to 54% RH, it should be noted that a short straight line occurs after a semicircle at low frequencies, and the straight line increases with the RH (75, 85 and 95% RH). The straight line was contributed to diffusion process of ions or charge carriers at the sensing material/electrode interface.³⁰ The ions contribute greatly to the conduction of sensitive material, which can be concluded from impedance values between 33% and 54% RH. At higher RH, more water molecules would be adsorbed by the polymer with quaternary phosphorus groups ionizing to P^+ and Br^- ions. The adsorbed water molecules make Br⁻ ions free against the interaction with the opposite charges P⁺. Therefore, Br⁻ ions could transfer freely and result in the decrease of the impedance. These results are consistent with that in Fig. 3, where the frequency shows little influence on impedance when RH is higher than 80%. This is because the



Fig. 5 Response and recovery curve of PTPPBr sensor between 11% and 95% RH (1 V AC, 100 Hz).



Fig. 6 Complex impedance plots of PTPPBr sensor under different humidity environments. ImZ, imaginary part; ReZ, real part.

ions (under high RH) could not follow the change of electric field under high frequencies.

It should be noted that the complex curve of the sensor at 11% RH is a part of a semicircle, which demonstrates the polymer could adsorb water molecules even at this low RH.31 This result is consistent with the high sensitivity of the sensor as shown in Fig. 3. The quaternary phosphorus groups could interact with water molecules due to the large quantity of polar P-Br bonds in the polymers. And since the polymer is formed of rigid framework, this electrolyte is different with the linear amphiphilic polymers or composites composed by polymer and organic salts. P⁺ spots are fixed in the polymer while Br⁻ spots exist in pairs with P⁺. The P⁺ and Br⁻ spots could interact with oxygen atoms (high electron density) and hydrogen atoms (low electron density) in water molecules respectively to form chemical adsorption layer (Fig. 7a). On the other hand, the cross-linked polymer is not soluble in the water, which means the interaction between the polymer and water molecules should be less strong than linear amphiphilic polymers. In addition, the P⁺ and Br⁻ spots are separately fixed in the polymer framework, so the adsorbed water molecules could not interact strongly with others and form large aggregates. What is more, the framework shows porous property, so water molecules could interact with the polymer quickly when the RH increases and the desorption process is also very fast when the RH decreases (Fig. 7b).

The long term stability of PTPPBr sensor was tested and the results are shown in Fig. 8. There is no obvious change for the impedances of the sensor under different RH after 120 days. The little fluctuation of the impedances in the long term operation demonstrates good stability of the sensor, which is important for practical applications. The good stability of PTPPBr sensor is considered to be contributed to the stable structure of the polymer network, because the network would not dissolve or loss even under high humidities.

It is really unexpected that the obtained cross-linked polymer based on a simple monomer shows very good humidity sensing properties as described above. The obtained porous amphiphilic polymer is a promising humidity sensing material, which



Fig. 7 (a) Illustration of the adsorption of water molecules and (b) schematic diagram of the transport of water molecules in the cross-linked polymer skeleton.



Fig. 8 The stability of PTPPBr sensor.

owns a stable organic network, quantitative and separated hydrophilic groups. And the structure of hydrophobic framework and hydrophilic group could be tuned by monomers for polymerization. Correspondingly, different porous polymers could be designed and their humidity sensitive properties could be controlled.

4. Conclusion

A nanoporous polymer with hydrophilic groups modified on the cross-linked hydrophobic framework was synthesized for humidity sensing. The polymer sensor showed good humidity sensing properties at whole humidity range, including a good linearity, little hysteresis, fast response and recovery and good stability. The cross-linked structure of the polymer is beneficial for the good stability of resultant sensor under long term operation. Our results provide a kind of promising material for humidity sensors.

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