

Investigation on the Ammonia Sensitivity Mechanism of Conducting Polymer Polypyrroles Using *In-Situ* FT-IR

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Abstract

Ammonia is toxic, colorless, and harmful to human health. It is important to detect ammonia effectively by gas sensors. In this paper, the mechanism of ammonia sensing on polypyrroles (PPy) films at room temperature has been investigated using a real-time, *in-situ* Fourier-transform infrared (FT-IR) spectroscopy. The introduction of ammonia results in a structural transformation of PPy films, which is confirmed by FT-IR spectrums. The structure and morphology of the products after the reaction between ammonia and PPy were investigated in detail by FT-IR spectrum and scanning electron microscope (SEM). It was found that the morphology of PPy films was changed to some degree after the reaction. Our results demonstrate that FT-IR spectroscopy is an extremely suitable technique for the characterization of the specific reaction between PPy and ammonia, since it allows monitoring the reaction at room temperature in real time. After the reaction between PPy and ammonia, the concentration of the carrier increases, and the resistance of PPy films decreases, indicating the sensitivity of detection of ammonia.

Keywords

Polypyrroles, Ammonia, *In-Situ* FT-IR, Electrochemistry

1. Introduction

Ammonia is toxic, colorless, pungent, and harmful to skin [1]. It is important to detect ammonia rapidly by gas sensors. Compared to traditional metal oxide materials, conducting polymers show obvious advantages for sensors, such as low price, good selectivity, and usage at room temperature [2] [3] [4] [5]. In the

1980s, doped polyacetylene was found to be good conductors [6] [7] [8] which drew large amounts of attention to the field of conducting polymers. Conjugated polymers, such as polyaniline (PAN) [9], polypyrroles (PPy) [10] and polythiophene (PTP) [11], become high conductive materials by doping. Researchers have adopted conducting polymers to detect toxic gases by gas sensors known as “electronic noses” [12] [13] [14]. PPy was chosen as the research object because of its facile synthesis, low electropolymerization potential, and good stability in air [15]. Chen and Li [16] have fabricated gas sensors based on PPy/silver composite nanotubes, which were found to be effective in response to ammonia (10 ppm).

A novel ammonia sensor with high surface-to-volume ratio PPy nanowire arrays was researched by Zhang [17]. Different PPy-coated/composited materials, such as TiO_2/ZnO [18], SnO_2 [19], ZnO [20], and other materials [21] [22] [23], to ammonia were researched and exhibited different sensitivities. Although various conductive polymer materials for gas sensors have been prepared by various methods [24] [25] [26], their working mechanisms have rarely been studied. Existing research [27] [28] indicated that polymer films had a complex redox reaction after the adsorption of gas, which decreased the conductivity of the polymer films. So far, however, there has been no uniform explanation of the sensitivity mechanism of conductive polymers.

The FT-IR spectrum is frequently used to investigate organics and shows great potential in the investigation on the mechanism of sensitivity change for organics. Carquigny *et al.* produced an ammonia gas sensor based on PPy films, and discussed the sensitivity mechanism using ex-situ FT-IR spectrum [29]. For better understanding the mechanism the real-time process of detection in sensitivity and the structure change of materials is highly desirable.

In this paper, conducting polymer PPy films were successfully prepared by an electrochemical in-situ polymerization method. The stable geometry of the PPy films enabled the films to maintain their original shape and structure during the ammonia testing. The interaction between PPy films and ammonia was then investigated, and the sensitivity mechanism was detected in real time and by in-situ FT-IR. An analysis of the FT-IR spectrum of PPy films before and after the flowing gas found that a chemical reaction occurred between the PPy films and the ammonia during the detecting process. The sensitivity mechanism of PPy films to toxic ammonia was studied at room temperature.

2. Experimental

2.1. Materials

Distilled pyrrole (Py, *Sinopharm Chemical Reagent Research Institute Co., Ltd.*) was dissolved under reduced pressure into acetonitrile (*Shanghai Chemical Reagent Co., Ltd.*), and KClO_4 (*Shanghai Chemical Reagent Co., Ltd.*) was dissolved in deionized water. The final solution is the mixture of the aforementioned solvents.

2.2. Characterizations

The morphology and the size of the as-prepared PPy films were characterized using SEM with the acceleration voltage of 10 kV (Sirion 200, manufactured by FEI, Holland).

FT-IR was applied to evaluate the functional group of PPy films. The FT-IR transmission spectra were obtained by using a FT-IR spectrophotometer (VERTEX 70, made by Bruker Co., Germany) in the range of 500 - 4000 cm^{-1} .

2.3. Preparation of the Substrate and the Polymer

Figure 1 shows the schematic of the fabrications process. The ceramic substrates (7 mm \times 6 mm printed interdigital gold electrodes) were cleaned by ultrasound for 10 min each in deionized water, ethanol and acetone, respectively, to remove surface dirt and oil stains; then the substrate was kept in deionized water and dried before being used [**Figure 1(a)**].

Initially, monomer pyrrole was added to acetonitrile to form a 0.1 M solution. Meanwhile, KClO_4 was dissolved into deionized water to form a 0.1 M solution. After 10 min ultrasonic dispersion for each solution, they were mixed together.

The potentiostatic polarization method was used in the polymerization process. The polarization voltage was 0.8 V and the polarization time was 2 hr. The working electrode and the auxiliary electrode were exchanged every 20 sec.

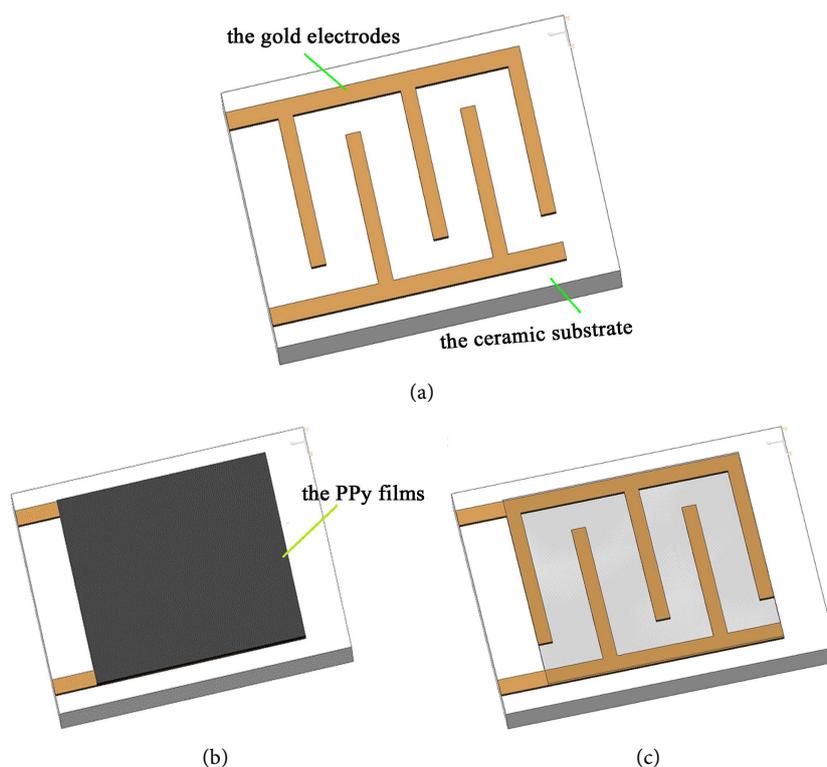


Figure 1. Schematic of the fabrication process (a) the ceramic substrates (b) and (c) after deposited.

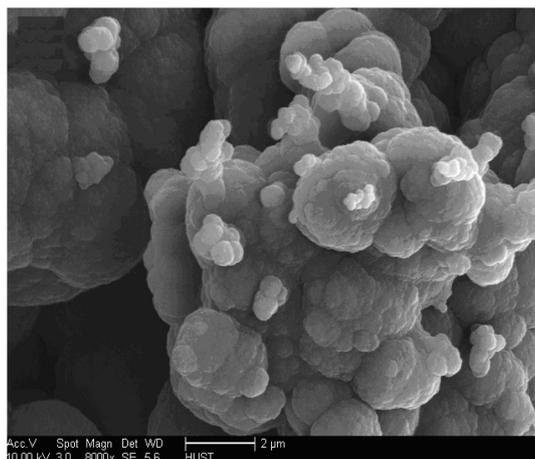
2.4. Ammonia Measurements

The sensitivities of PPy films were tested in different concentrations of ammonia. A 30 L container with a removable lid served as a test chamber, as the sensor could be set within. The films were statically exposed in the gas after the liquid evaporated. The sensitivity was defined as $(R_0/R_1) \times 100\%$ (R_0 = the initial resistance and R_1 = the tested resistance).

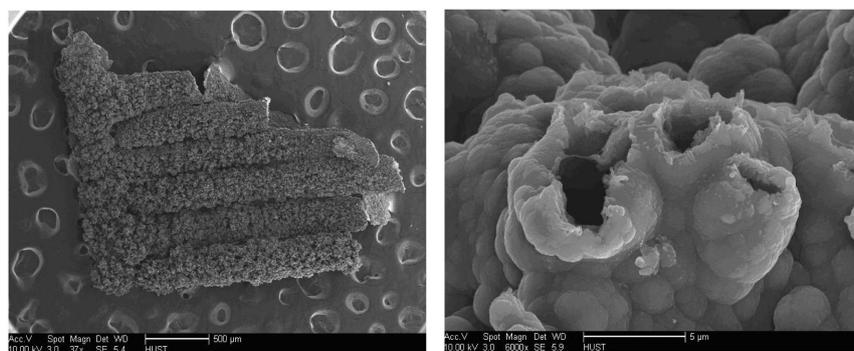
3. Results and Discussion

3.1. Morphological Characterization

Figure 2(a) shows the SEM micrograph of the PPy films produced by the electrochemical *in-situ* polymerization method. It is apparent that flower-like particles are obtained. **Figure 2(b)** shows the image of the PPy films, which is alternately deposited on the interdigitated golden electrodes. It can be concluded that the films firmly adhere to the golden electrodes. After desorption of the ammonia, the morphology of the PPy films is changed. Holes appear among the initial compacted thin films [**Figure 2(c)**]. It can be presumed that a reaction between PPy films and ammonia occurs.



(a)



(b)

(c)

Figure 2. SEM images of the PPy films (a) as synthesized (b) deposited on the gold electrodes (c) after desorption of ammonia.

3.2. Sensitivity to Ammonia

The sensitivity feature of the sensor in 800 ppm ammonia is shown in **Figure 3**. The resistance of PPy films decrease after ammonia fills the container. The sensitivity time is less than 15 s and the recovery time is about 100 s. When the ammonia comes in contact with the PPy films, physical adsorption occurs between them in a complex chemical reaction, which results in a decrease in the resistance of the film. When PPy films were placed in ammonia, ammonia could be adsorbed and diffused on the films. Ammonia is a kind of reducible gas which is able to provide electrons, and increases the electron concentration of PPy films. Therefore when ammonia contacted the PPy films, the resistance of the PPy films decreased. As the result of incomplete reversible reaction, the resistance of PPy films did not recover to the original value [30].

With the increase of ammonia concentration, the resistance of the films decreased, as shown in **Figure 4**. As the result of limited recovery time and incomplete reversible reaction, the resistance of the PPy films did not return to the original value. As the concentration of ammonia increased the sensitivity of the films increased, as shown in **Figure 5**, it can be seen that the sensitivity of PPy films is only 120% in 100 ppm ammonia. When the gas concentration changed from 300 ppm to 500 ppm, the sensitivity of the PPy films increased from 180% to 250%. From the data in **Figure 5**, it can be concluded that the relation between the sensitivity and the concentration is almost linear.

Figure 6 shows a typical sensitivity-recovery curve obtained for 500 ppm ammonia. To investigate the recovery ability of PPy films in ammonia, eight continuous sensitivity tests were conducted in 500 ppm ammonia. The resistance of the films gets back to the initial value, which leads to the conclusion that this material has enough stability for continuous detecting in ammonia.

Figure 7 shows the sensitivities of PPy films 8 trials in 500 ppm ammonia. By comparing the eight sensitivities, it can be deduced that the test has good reliability, and that this material also possesses competitive gas sensing characteristics, thus PPy films can be used to test ammonia for commercial purposes.

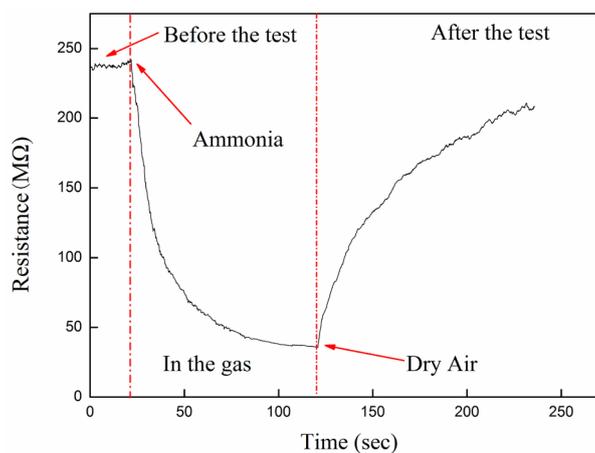


Figure 3. Resistance—time curve in 800 ppm ammonia.

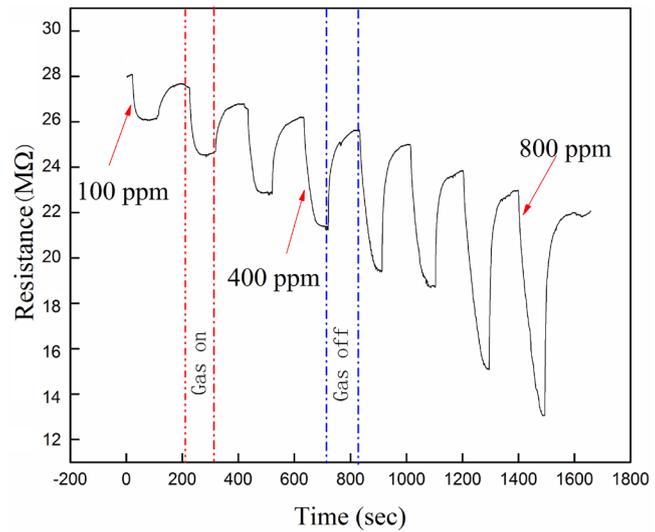


Figure 4. Resistance—time curve in different concentration ammonia.

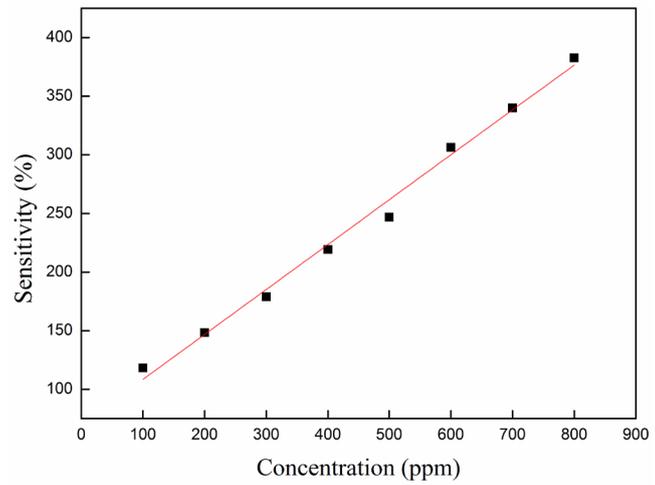


Figure 5. Sensitivity of PPy film in different concentrations of ammonia.

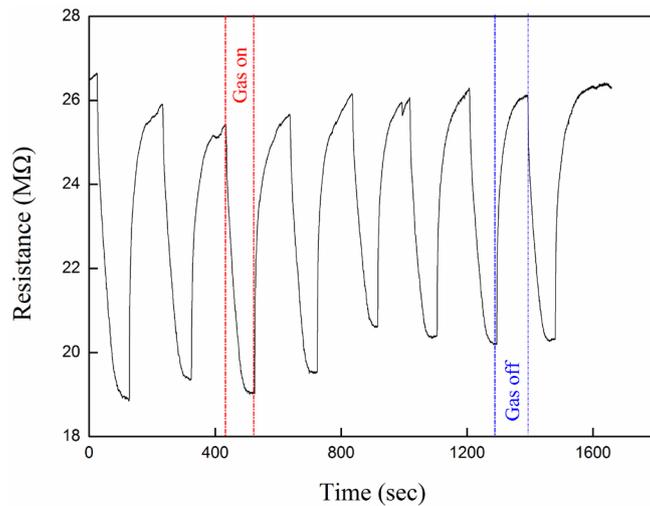


Figure 6. Resistance—time curve of 8 retests in 500 ppm ammonia.

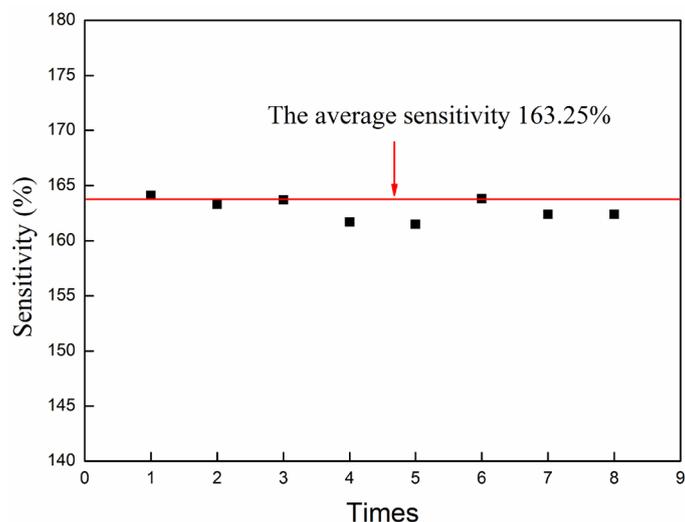


Figure 7. The sensitivities of PPy films 8 trials in 500ppm ammonia.

3.3. Sensitivity Mechanism

In order to discuss the sensitivity mechanism between PPy films and ammonia, we designed the experiment that the process was in-situ monitored by FT-IR spectroscopy. PPy films were placed in the ammonia flow for 2 min, during which FT-IR spectrums were used to scan at intervals of 10 sec.

In **Figure 8**, we present the FT-IR plural spectra of PPy films before, during and after the detection process. In **Figure 8(a)**, the peak in 1650 to 1150 cm^{-1} can be assigned to the symmetric/asymmetric C=C/C-C vibrations. From the band at 960 cm^{-1} , we conclude that PPy films are doped with ClO_4^- . The band at 1300 cm^{-1} is attributed to the C-N stretching vibration modes. These would account for the presence of the pyrrole ring after electrochemical polymerization.

Figure 8(b) shows the FT-IR spectrum of PPy films after the adsorption of ammonia. Compared with **Figure 8(a)**, two broad adsorption bands appear when PPy films are exposed to ammonia flow. The first band at 3340 cm^{-1} is assigned to ammonia. After the adsorption of ammonia, PPy chemically reacted with the ammonia. As the band at 1600 cm^{-1} is assigned to amino, we proposed that by losing electrons, ammonia becomes amino, attaching to the main chain of PPy.

Figure 8(c) illustrates the FT-IR spectrum of PPy films after desorption of the ammonia. There is no band at 3340 cm^{-1} , indicating that the reaction between PPy films and ammonia is reversible. Compared with **Figure 8(a)**, the main groups of infrared characteristic absorption peaks have returned to their original positions, but some bias still exists, which indicates that the reaction is not fully reversible. In addition, a lot of infrared absorption peaks disappear in the band at 1600 cm^{-1} due to the disappearance of the amino.

In order to further illustrate the sensitivity mechanism between ammonia and PPy films, the adsorption process was investigated by real-time FT-IR spectrometer. **Figure 9** shows the FT-IR plural spectra of PPy films in ammonia with

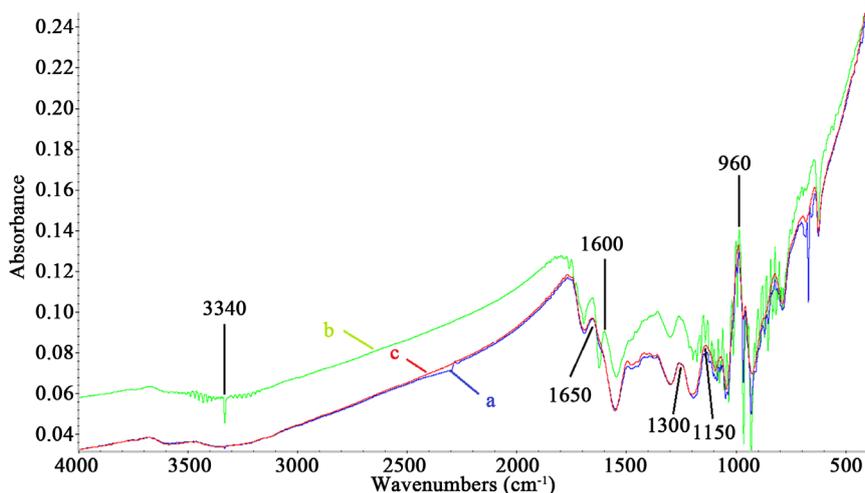


Figure 8. FT-IR plural spectra of PPy films (a) before adsorption of ammonia (b) during adsorption of ammonia and (c) after desorption of ammonia.

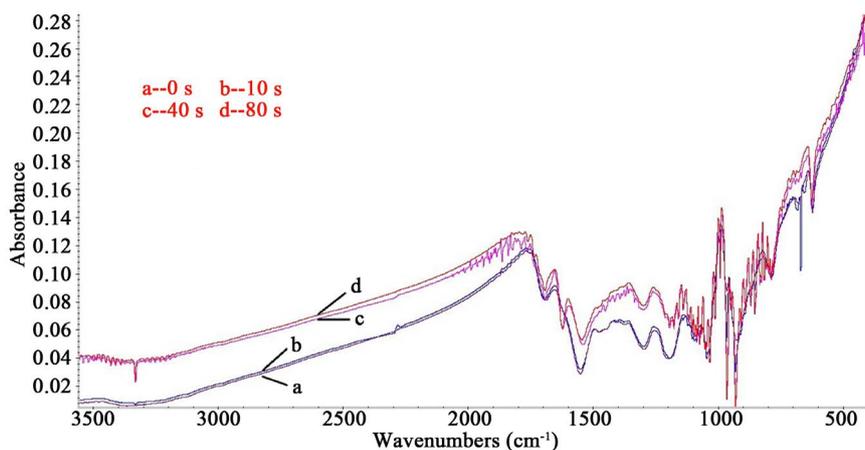
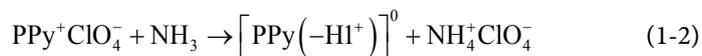


Figure 9. FT-IR plural spectra of PPy films in ammonia with different times.

different times. When ammonia contacted PPy films, physical adsorption occurred first. A tiny peak at 3340 cm^{-1} appears in **Figure 9(b)**. As result of the reducibility of ammonia, PPy films receive the electrons. The lost electrons, which do not belong to any atoms, attach themselves to the π -conjugated carbon chains. This leads to the change in the film conductivity, with the resistance of PPy films decreasing. The obvious band at 1600 cm^{-1} appears in **Figure 9(c)** and **Figure 9(d)**. The reaction process is shown in **Figure 10**.

There were two kinds of reaction mechanism between PPy films and ammonia. The cases are shown in 1-1 and 1-2.



As shown in **Figure 8(b)**, the band at 1600 cm^{-1} is assigned to amino. By losing electrons, ammonia becomes amino, attaching to the main chain of PPy. We proposed that there are the simple compensation effects involving electron

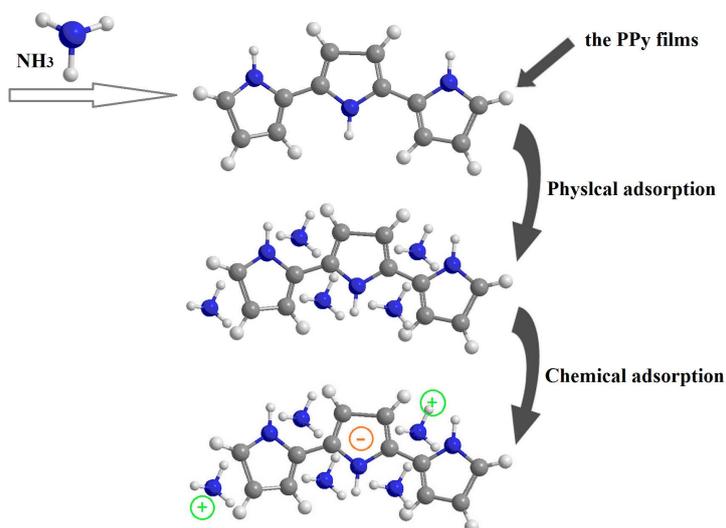


Figure 10. Schematic of the reaction process between PPY films and ammonia.

transfer. In electron transfer compensation, ammonia molecules compensated the PPY films charge, which caused changes in the electrical conductivity of the PPY films. The results proved that there is direct evidence for the first case.

4. Conclusions

The conducting polymer PPY films were successfully prepared by an electrochemical *in-situ* polymerization method. The sensitivities of PPY films to different concentrations of irritant ammonia were tested at room temperature. The interaction between PPY films and ammonia were studied by real-time, *in-situ* FT-IR spectrometer. The results indicated that redox reactions took place between the PPY film and ammonia, causing changes in the electrical conductivity of the PPY films. As the donor to PPY films, the electrons of ammonia contributed to the increase of electron concentration in PPY films, thus the resistance of the films decreased. The results showed that in a certain range of concentration of ammonia, there was a good linear relationship for the concentration of ammonia and sensitivity.

Based on these results, the conducting polymer PPY is promising for the detection of ammonia. The research work is insufficient, not detecting the other gases. We hope that this work is helpful for further exploring more PPY-based materials with even novel sensing performance for NH_3 sensing at room temperature.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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