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Comparison of NO_2 and NH_3 gas adsorption on semiconductor polyaniline thin films

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Semiconductor polyaniline (PANI) thin films have proven to be an optically sensitive element for detecting gaseous NH_3 and NO_2 at room temperature. Although the absorption of either of them on PANI films results in the color change of the films, from green to blue, the mechanism of the interaction of each gas with the polymer is different. Ultra-violet (UV)-Visible (VIS) spectra of the NO_2 saturated PANI thin films give an increasing blue shift of the polaron band (1.5 eV) as a function of the gas concentration. The NH_3 gas saturated PANI samples, however, show a small red shift of the same absorption band and a slight increase of the relative intensity of the 2.0 eV band. It is suggested that NO_2 oxidizes the semiconductor PANI just as this can be oxidized by an electrochemical potential in an aqueous acid solution, whereas NH_3 deprotonates the polymer without taking out any electrons from it. The presence of NH_4^+ and of NO_2^- species in the gas saturated PANI samples is shown by the analysis of their Fourier Transform Infrared (FT-IR) spectra.

Keywords: Polyaniline thin films; NO_2 and NH_3 gas detection; UV-VIS and FT-IR spectra.

Se han comprobado que las películas delgadas de polianilina (PANI) son elementos ópticamente sensibles para detectar a los gases de NO_2 y NH_3 a temperatura ambiente. Aunque el resultado de la adsorción de ambos gases resulta en el cambio de color de las películas, de verde a azul, el mecanismo de interacción de cada uno con el polímero es distinto. Los espectros de ultravioleta (UV)- visible (VIS) de las películas delgadas de PANI saturadas con NO_2 muestran un desplazamiento de la banda polarónica (1.5 eV) hacia el azul como función de la concentración del gas nocivo. En cambio las muestras de PANI saturadas con el gas amoniaco indican un corrimiento de la misma banda hacia el rojo y un incremento ligero de la intensidad relativa de la banda de 2.0 eV. Esto sugiere que NO_2 oxida al semiconductor PANI de la misma forma que un potencial electroquímico en una solución ácida acuosa, mientras que NH_3 desprotona al polímero sin quitarle ningún electrón. La presencia de las especies adsorbidas de NH_4^+ y NO_2^- en las muestras de PANI saturadas con los dos gases se puede observar en sus espectros de infrarrojos por Transformada de Fourier (FT-IR).

Descriptores: Películas delgadas de polianilina; detección de gases de NO_2 y NH_3; espectros de UV-VIS y FT-IR.

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1. Introduction

Polyaniline (PANI) is one of the conducting polymers that changes its electrical and optical properties as a function of the molecular structure. PANI has been shown to be an electrochromic, electromechaniced and capacitive material, a chemical sensitive element at room temperature, a stable organic semiconductor, etc. As a gas sensing material, PANI has been studied for the detection of NO_2 [1-3], NH_3 [4-10], H_2O [11-12], toluene [13], methane [14], CO_2 [15], H_2S [1], and HCl [16]. It has also been studied as a chemical sensor for pH measurement [17-21], antibody detection [22], urea sensing [23], glucose estimation [24-25], aliphatic alcohol detection [26], detection of low concentrations of Cu^{2+} and Pb^{2+} in electrochemical sensors [27], and as a amperometric sensor element [28]. In our laboratory, PANI thin films have been used in an optochemical sensor system to detect NH_3 [29,30] and NO_2 [31] gases at very low concentrations at room temperature in air. Although the absorption of both NH_3 and NO_2 on PANI causes a color change of the films from green to blue, the tone of the blue color is different in each case. Secondly, it is observed that the optical transmittance change of PANI samples is much more sensitive to NO_2 than to NH_3, but its desorption rate is much lower than that of the ammonia gas in a dried ambient. Only the presence of ambient humidity or the heating of the NO_2 absorbed samples could accelerate the NO_2desorption from the PANI samples.

The absorption of the two gases mentioned on PANI induces a change in the electronic structure of the polymer. Since the discovery of semiconductor properties of PANI as a function of its molecular structure, it has generally been accepted that the polymer changes its electronic structure either by a redox reaction or by a protonation-depronation process. There are three basic forms of PANI: leucoemeraldine base (transparent or yellow, LEB), emeraldine base (blue, EB) and pernigraniline base (dark blue, PNB). LEB is the most reduced product, and PNB the most oxidized. EB falls somewhere between them. The protonation of EB or the oxidation of LEB can lead to the formation of a semiconductor or conductor state of PANI: emeraldine salt (ES), which is a green product and can be obtained by the oxidative polymerization of aniline either chemical or electrochemically in an acidic medium. From electrochemical analysis, it is shown that the oxidation state of ES is higher than LEB but lower than EB.

The reaction between NO_2 and semiconductor thin films of PANI(ES) should result in the oxidation of ES and reduction of NO_2. Reference 32 found the reduced NO_2^- molecules on polypyrrole samples used as the NO_2 gas sensing element. So one expects to find an oxidized PANI(ES) using NO_2 gas, which could be PANI(EB) or even PANI(PNB), or a mixture of both. In the case of NH_3, this should deprotonate the ES to convert it into EB and NH_4^+ should be the most probable species to be formed on PANI films, according to Ref. 33. In this work, we try to analyze the UV-VIS absorption spectra of NO_2 and NH_3 saturated PANI(ES) films to visualize the oxidation process of PANI by different gases and confirm the existence of the absorbed species on PANI by FT-IR spectroscopy.

2. Experimental

Chemically deposited polyaniline (PANI) and PANI-poly(2-acrylamido-2-methyl-1-propanosulfonic acid) (PAMPS) composite thin films were obtained under the same conditions as reported in a previous work [34]. Briefly, doubly distilled aniline monomer (J.T. Baker) was dropped into a stirred 2 M HCl aqueous solution at a temperature of about 3°C. Then a cooled (5-10°C) 0.1 M $(NH_4)S_2O_8$ aqueous solution was slowly added to the monomer solution with vigorous stirring for the polymerization of aniline. After that, clean polymethyl methacrylate (PMMA) sheets were introduced into the solution bath and thin films of a green color were obtained after 1 hour of immersion. The film thickness was estimated to be about 200 nm by Atomic Force Microscopy (Autoprobe CP, Park Scientific).

NH_3 and NO_2 gas sensing experiments were carried out at room temperature on a dc-nulling optical transmittance bridge system, with a PANI thin film sample as the sensing element, as reported in Refs. 29 to 31. The testing gas was diluted in a pure, dried N_2 gas, which was also used as the carrier gas. The resolution of the optical setup was estimated to be about $(\Delta T/T)_{min} \sim 10^{-4}$ [31], where T is the optical transmittance of the film measured at about 630 nm. The sensitivity of the system depends on the sensing gas. In the case of NO_2, the optical system can detect a gas concentration much lower than 1 ppm.

Ultra violet-visible (UV-VIS) spectra of the polymer films deposited on PMMA substrates were recorded on a Shimadzu UV160U spectrophotometer. Those of the NO_2 (1000 ppm) and NH_3 vapor saturated PANI and PANI-PAMPS thin film samples were recorded ex-situ immediately after the exposure to the testing gases. Then they were used to form KBr pellets for FT-IR spectrum measurements on a Perkin-Elmer FT-IR 1605 spectrophotometer in the transmittance mode.

3. Results and Discussion

Figure 1 shows the optical transmittance changes of PANI thin films exposed to a dried 3 ppm of $NO_2$and a 600 ppm of NH_3 gas flux. It is observed that PANI films are very sensitive to NO_2 gas; a few ppm or even ppb concentration of the gas is sufficient to cause a marked optical transmittance change in this polymer detected by the optical sensing system. However, the desorption of the same gas is a slow process when a dried N_2 or air flux is introduced into the testing chamber as the purging gas. Only the return of ambient humidity could produce an appreciable recovery towards the original optical transmittance of the films as a consequence of the desorption process of NO_2 from polymer samples (Fig.1(a)). On the other hand, the absorption-desorption process of NH_3 on PANI samples is much more reversible (Fig.1(b)). A dynamic equilibrium is established between the sensing gas and the semiconductor thin film, and the desorption rate of the NH_3 from PANI is complete and much more rapid than NO_2 with a dried N_2 purging gas. The comparison between the optical change values on PANI films caused by the absorption of these two gases leads to the suggestion that NO_2 interacts much more strongly with PANI than does NH_3.

As mentioned in Sec. 2, our PANI and PANI-PAMPS thin films were obtained on the state of emeraldine salt (ES). According to Brédas [35], the theoretical prediction of the electronic structure of ES has shown good agreement with the experimental optical absorption spectra. The most probable electronic structure of PANI(ES) is the polaron lattice with a single, half-occupied defect band within the gap. The direct optical transitions from the upper occupied valence band to the polaron band are calculated to be at 1.8 eV, which compared favorably with the first optical absorption at about 1.5 eV. The direct optical transitions from the second upper occupied valence band to the polaron band are calculated to

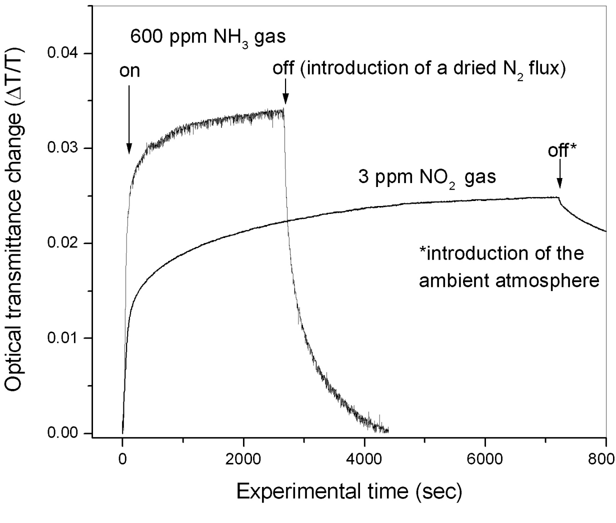

FIGURE 1. Optical transmittance kinetic curves at about 630 nm of PANI thin films exposed to a continuous dried (a) 3ppm NO_2 and (b) 600 ppm NH_3 flux. For desorption process the purging gas was (a) a dried N_2 flux and (b) ambient atmosphere.

be at 2.6 eV, which is in good agreement with the second absorption at 2.8 eV. The first electronic transitions from the upper defect band and the conduction band are predicted to occur at 4.1 eV, in agreement with the location of the third absorption. In Figs. 2 and 3, the ES absorption bands at around 1.5 eV (820 nm) and 2.9 eV (425 nm) are clearly observed in our original PANI(ES) and PANI-PAMPS films. The introduction of PAMPS in PANI causes a slight change on its absorption spectra shape, but maintain the basic electronic transitions of PANI.

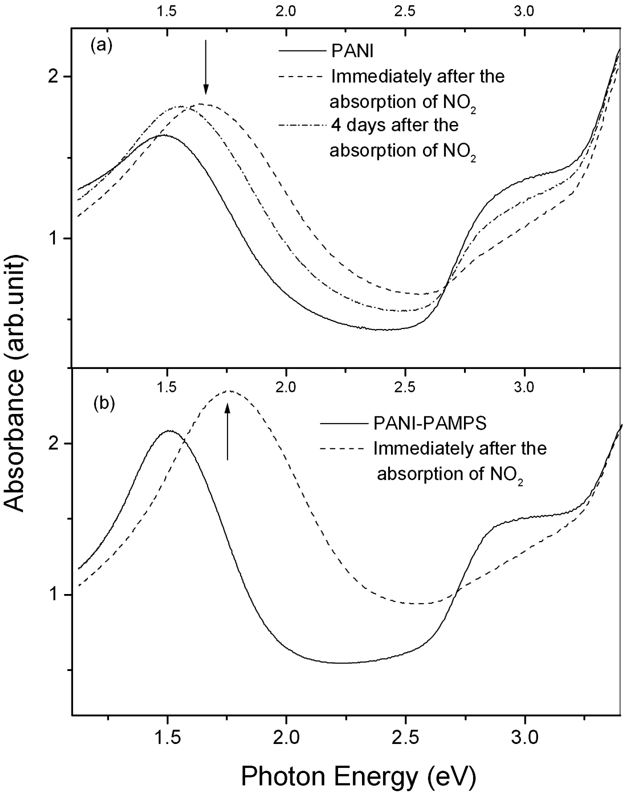

FIGURE 2. Optical absorbance spectra of the same samples of PANI and PANI-PAMPS thin films before and after exposure to a 1000 ppm NO_2 gas.

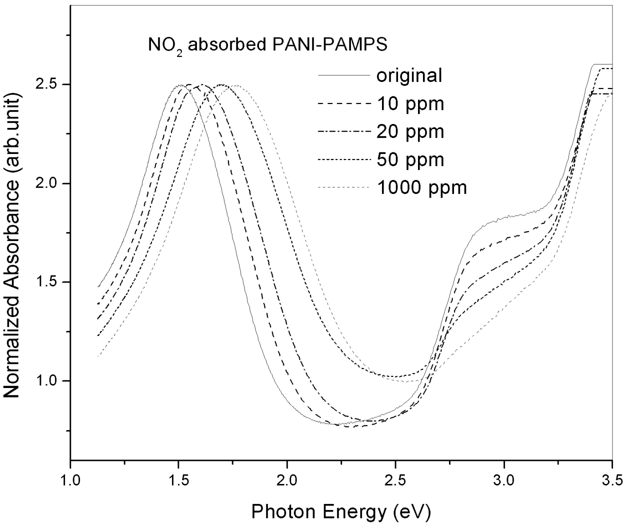

FIGURE 3. Normalized optical absorbance spectra of PANI-PAMPS thin film samples exposed to NO_2 gas flux of different concentration.

Figure 2 shows UV-VIS spectra of PANI and PANI-PAMPS films before and immediately after being saturated with a NO_2 gas of 1000 ppm. The films changed color from green to dark blue. The electronic structure of the polymer is clearly modified: the 1.5 eV band blue shifted to 1.65 eV for PANI and to around 1.75 eV for PANI-PAMPS samples. The decrease in intensity of the band around 2.9 eV is a strong suggestion of the interaction between the the polaron sites and the unpaired oxygen electron of the NO_2 molecule. After four days of being stored in ambient conditions, the intensity of these two bands in PANI samples partially recovers its original value, which means that the desorption process of NO_2 from PANI is kinetically slow. As shown in Fig. 3, the blue shift of the 1.5 eV band increases with the NO_2 gas concentration: 1.55 eV for 10 ppm, 1.63 for 20 ppm and 1.7 eV for 50 ppm of NO_2 gas in the case of PANI-PAMPS samples. It implies that this blue shift should be related to the amount of absorbed NO_2 molecules on PANI. A similar effect is observed with the intensity of the absorption band at 2.9 eV which decreases as a function of the NO_2 concentration and practically disappears when exposed to 100 ppm of NO_2.

In order to clarify the origin of these changes, it is convenient to relate the UV-VIS absorption spectra of PANI samples to their redox properties. In an aqueous acidic medium, PANI films show different oxidation states at different applied potential; they are LEB (transparent or slightly yellow) at a voltage interval of -0.2 to 0.0 V (vs. Ag/AgCl), ES (green) at 0.2 to 0.4 V, EB (blue) at 0.4-0.6 V, LNB (intense blue) at 0.6 to 0.8 V. More than 0.8 V (vs. Ag/AgCl) the films become overoxidized (violet). It was observed that the original spectrum of the PANI(ES) green film shown in Fig.2 (and Fig. 4) was the same as that of the PANI film in the acid medium measured at 0.2 to 0.4 V (vs. Ag/AgCl) reported by Nekrasov *et al.* [36]. And the absorption spectra of NO_2 absorbed PANI films show a very similar oxidation tendency as a function of NO_2 gas concentration (Fig. 3) compared with those of the PANI films electrochemically polarized from 0.2 to 0.8 V (vs. Ag/AgCl) reported in Ref. 36. Therefore, it seems that PANI thin films were oxidized by NO_2 gas and consequently electrons should be transferred from PANI to NO_2 to form the absorbed species, NO_2^-. The 1.5 eV absorption band shifts to blue as the concentration of the absorbed gas increases, implying that the degree of oxidation increases with the gas concentration. This can be justified if we think that a larger concentration of NO_2 gas implies more absorbed NO_2 molecules on PANI and consequently a major amount of electrons transferred from the polymer to NO_2.

The correlation of the gradual blue shift of 1.5 eV of PANI(ES) with the increase of the applied electrochemical potential in an acidic medium is made in Ref. 36, based on the so-called Alentsev-Fock method. It presupposes the separation of the individual absorption bands in an electronic or luminescent spectrum. In that paper, the spectroelectrochemical data of PANI samples have been recorded at different potential values. The authors claim that the gradual change of the potentials causes the gradual change of the polymer structure accompanied by the gradual change of portions of individual spectral components in the integral spectrum. In the case of NO_2 gas absorption on PANI, it is reasonable to assume a gradual change in electronic structure of the polymer as a function of the concentration of the testing gas.

In the same way, Fig. 4 shows UV-VIS spectra of PANI and PANI-PAMPS thin films exposed to a saturated NH_3 vapor. The color of the ES films was also changed, but from green to a lighter blue than that of the NO_2 saturated PANI. Since the desorption rate of NH_3 from PANI was fast in air, the ex-situ absorption spectra of NH_3 saturated PANI and PANI-PAMPS films show much smaller but also appreciable changes: a slight increase of the band at around 2 eV, and the decrease in the intensity of the 1.5 and 2.9 eV bands (except for PANI-PAMPS, in which the 2.9 eV band is slightly increased). However, compared with the NO_2 absorbed PANI films, the absorption of NH_3 on the same polymer induces a different absorption spectrum change (Fig. 4). Although the absorption of ammonia causes the same color change in PANI films, their UV-VIS spectra do not show a blue shift in the 1.5 eV band. Instead, a small red shift of the 1.5 eV band and a slight increase in the absorption intensity around 2.0 eV (620 nm) can be seen in the spectra.

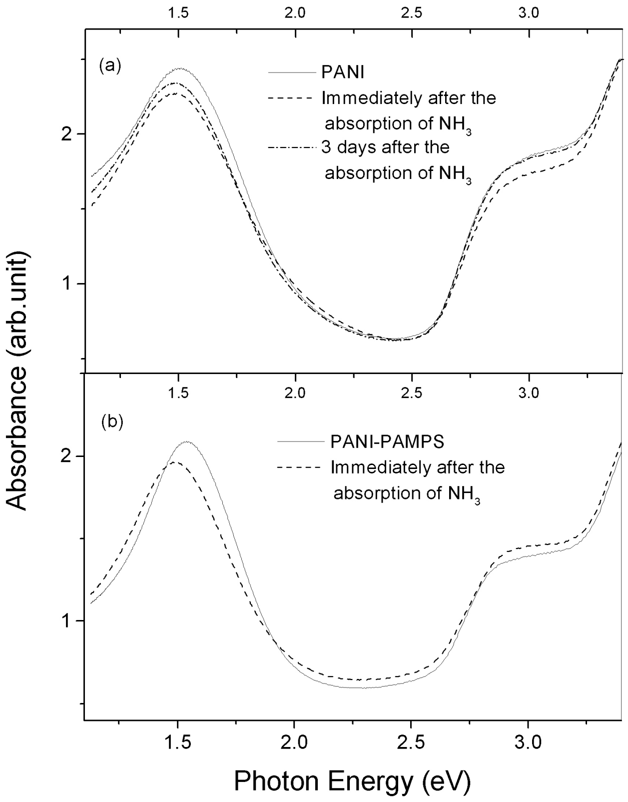

FIGURE 4. Optical absorbance spectra of the same samples of PANI and PANI-PAMPS thin films before and after exposure to a saturated NH_3 vapor.

The increase in the 2.0 eV band (without the blue shift of the 1.5 eV) is a signal of an increase in the EB state. Experimentally, it is known that the absorption spectra for EB give basically two broad peaks: (1) 3.9-4.0 eV absorption assigned to a $\pi - \pi^*$ transition, and (2) the second one observed at around 2 eV [29,37,38]. However, the origin of this band is not clear from the theoretical point of view. It is believed that the 2.0 eV band comes from the charge transfer exciton formed by the transition of benzenoid to an adjacent quinoid group [38,39]. Since PANI(ES) can also be converted to PANI(EB) via deprotonation instead of the redox process, it suggests that the transition from ES to EB as a consequence of deprotonation of ES and the formation of NH_4^+ species on PANI films, as already suggested in Ref. 33. Furthermore, the slight red shift and decrease in the 1.5 eV band in these samples should be the consequence of a decrease in of polaron populations. The fast desorption of NH_4^+ from PANI is due to the decomposition of NH_4^+ into NH_3 in air [33].

Curiously, the polemic 2.0 eV band observed in EB samples is also present in the oxidation process of LEB thin films in air [40]. It is known that LEB is an insulator with a large bandgap, showed the onset of a $\pi - \pi^*$ transition around 3 eV, with a peak o 3.7-3.8 eV [37]. However, an increase in the 2.0 eV band was observed as a consequence of the slow oxidation of the LEB in air during more than one day and the fact that the film finally presented a violet color [40]. This oxidation process is very similar to the oxidation of PANI(ES) by NO_2 gas, but with a clear difference in the UV-VIS spectra. An explanation for the 2.0 eV band is given in Ref.[40] as a consequence of the formation of the bipolaron band, which is still under discussion.

To test the existence of the NO_2^- and NH_4^+ absorbed species on PANI thin films, FT-IR spectra of the testing gas saturated PANI and PANI-PAMPS thin film samples are shown in Figs. 5 and 6, respectively. There are some common characteristics in NO_2 absorbed samples when compared with the original PANI samples: (1) the relative intensity of 3400 cm^{-1}, 2950 cm^{-1} and 1300 cm^{-1} bands is increased, and (2) a new band at 1604 cm^{-1} appears. As mentioned in the literature, the IR active bands at around 3400 cm^{-1} should be related to the stretching of NH groups in PANI groups [41], in particular those NO_2 molecules that, when associated with NH groups, show the NH stretching band at 3300 cm^{-1}, and antisymmetric and symmetric stretching bands of NO_2 at 1580 and 1300 cm^{-1}, respectively [41]. Thus the increase in the relative intensity of the 3400 cm^{-1} band in NO_2 absorbed PANI samples could be explained by the increase in the interaction between positively charged NH groups of PANI with negatively charged NO_2 species. And the appearance of the 1604 cm^{-1} band and the increase in the relative intensity of 1300 cm^{-1} band also indicate the presence of NO_2 molecules in the PANI samples.

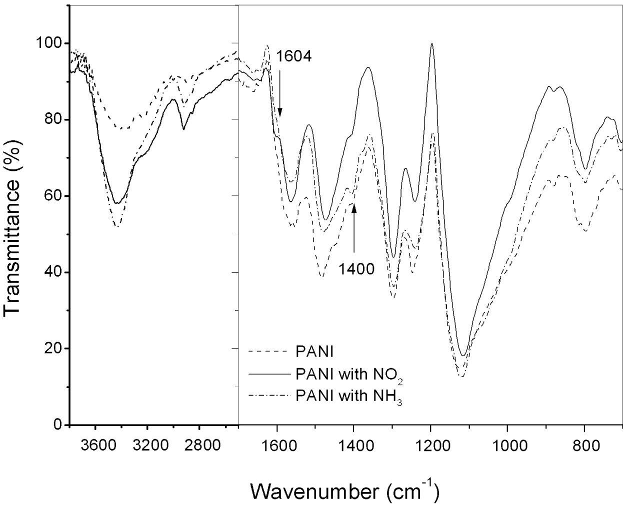

FIGURE 5. FT-IR spectra of PANI thin film samples: (a) an original, (b) after exposed to a 1000 ppm NO_2 gas, and (c) after exposed to a saturated NH_3 vapor.

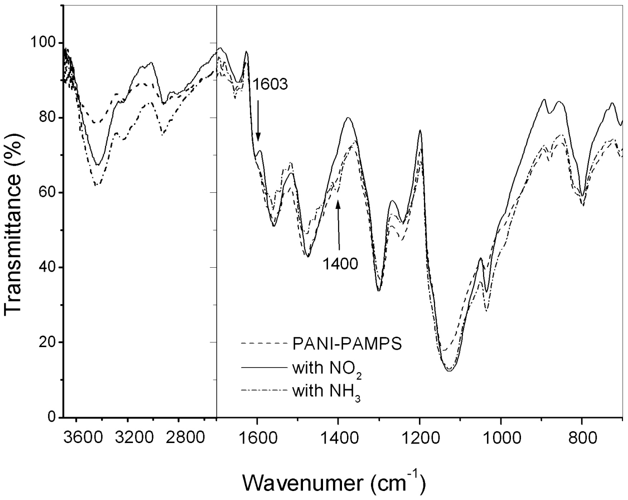

FIGURE 6. FT-IR spectra of PANI-PAMPS thin film samples: (a) an original, (b) after exposed to a 1000 ppm NO_2 gas, and (c) after exposed to a saturated NH_3 vapor.

On the other hand, the band at around 2950 cm^{-1} should be the C-H stretching of aromatic rings of PANI. According to Ref. 42, a good indication of the interaction of a dopant anion in PANI can be obtained by examining the spectroscopic regions which encompass the amine groups and the C-H bands of the benzene rings. These bands should be very sensitive to anion interaction because they are sensitive to hydrogen bonding and electron density changes based on the introduction of electron donating or withdrawing groups within the polymer. At the same time, the N-H region also shows a dependence on the doping anion. Anions which typically form hydrogen bonds with amine groups show variations in the intensity and shape of the N-H band. Consequently, the increase of the relative intensity of 3400 cm^{-1} (N-H) and 2950 cm^{-1} (C-H) bands in the NO_2 absorbed PANI samples should lead to the suggestion of some kind of interactions between amine groups of PANI and absorbed NO_2 species on the polymer. Furthermore, according to Refs. 37 and 42 the degree of oxidation of PANI can be estimated by calculating the ratio of the intensity of the $\sim$1570 cm^{-1} band (C=C stretching of quinoid) to that of the 1500 cm^{-1} band (C=C stretching of benzenoid). Figure 5 shows clearly that a NO_2 absorbed PANI thin film is more oxidized than the original PANI and NH_3 absorbed PANI film samples.

The absorption of NH_3 molecules on PANI and PANI-PAMPS samples is also shown. The most notable difference between the NH_3 absorbed and other PANI samples is the formation of a shoulder at around 1400 cm^{-1}, together with an increase in the relative intensity of 3400 cm^{-1}. According to Ref. 41, the ammonium ion shows vibrational bands at 3332-3100 cm^{-1} (NH_4^+ stretching) and 1484-1390 cm^{-1} (NH_4^+ deformation), in particular the antisymmetric stretching band of NH_4^+ in $NH_4^+Cl^-$ is at 3200 cm^{-1} and the deformation of NH_4^+ is at 1410 cm^{-1}. On the other hand, NH_3 vapor shows its multiple and very sharp absorption bands at around 3350, 1630 and 1200-800 cm^{-1} as a substance in its gaseous phase. Consequently, the new band at 1400 cm^{-1} looks much more like a coordinated compound of NH_4^+ than a free molecule of NH_3, so the appearance of this band should be related to the formation of NH_4^+ on PANI. It is worth mentioning that the stretching band of NH_4^+ compounds should be at around 3200 cm^{-1}, which is clearer in PANI-PAMPS than in PANI single samples. Finally, the increase in the relative intensity of the 3400 cm^{-1} and 2950 cm^{-1} should also be the result of a strong interaction between the absorbed NH_3 molecules and the NH and CH groups of PANI, as mentioned in Ref. 42.

4. Conclusions

From UV-VIS studies on NO_2 and NH_3 saturated PANI and PANI-PAMPS thin film samples, one concludes that NO_2 molecules oxidize polymers similary to the way an electrochemical potential does. The degree of oxidation of the polymers increases with the gas concentration, which indicates that more electrons were transferred from NO_2 molecules to PANI chains. On the other hand, the interaction with NH_3 gas results in the appearance of the absorption band of emeraldine base of PANI, a deprotonated form of the original emeraldine salt of the same polymer. The vibrational absorption spectra of the gas saturated PANI samples indicate the presence of a strong interaction between nitrogen atoms of the two gases and the amine rings of PANI, as well as the stretching bands of NO_2 and NH_4 compounds. It indicates that they were present in PANI and PANI-PAMPS samples.

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