

# Thermally assisted NO<sub>2</sub> and NH<sub>3</sub> gas desorption process in a polyaniline thin film based optochemical sensor

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NO<sub>2</sub> gas is a strong electron acceptor that can oxidize the chemically deposited semiconductor polyaniline (PANI) at room temperature under atmospheric pressure. Since each redox state of this polymer is associated with a specific electronic structure, an oxidized PANI thin film undergoes a color change that can be detected in a sensitive optochemical sensor. But the strongly absorbed NO<sub>2</sub> molecules cannot be removed at room temperature from the polymer material during the purging process with a dried N<sub>2</sub> gas flux. We report in this work that a heating element can be integrated into the optochemical sensor to elevate the sensing sample temperature during the desorption process. At temperatures higher than 50°C, the optical signal of the NO<sub>2</sub> absorbed PANI samples starts to return to its original value during the purging process, suggesting the desorption of the NO<sub>2</sub> species from the PANI samples. The higher the heating temperature, the greater the activation energy for desorption, and consequently the faster the desorption speed. Similar results are also obtained for the NH<sub>3</sub> desorption process occurring in the same polymer.

**Keywords:** Polyaniline thin films; NO<sub>2</sub> desorption process; activation energy for desorption; optochemical sensors.

El gas NO<sub>2</sub> es un fuerte aceptor de electrón que puede oxidar la película de polianilina (PANI) depositada químicamente a temperatura ambiente bajo presión atmosférica. Como cada estado de redox de este polímero está asociado con una estructura electrónica específica, el proceso de absorción de NO<sub>2</sub> que ocurre en una película de PANI puede detectarse fácilmente por el cambio de su color en un sensor optoquímico. Sin embargo, se ha observado que las moléculas absorbidas de NO<sub>2</sub> en PANI no se pueden remover fácilmente durante el proceso de purgación con un flujo seco de N<sub>2</sub> a temperatura ambiente. En este trabajo se reporta que se pudo integrar un elemento de calentamiento dentro del sensor óptico para elevar la temperatura de la muestra de sentido durante el proceso de desorción. Se conoce que a temperaturas mayores que 50°C, la señal óptica de las muestras de PANI con moléculas de NO<sub>2</sub> absorbidas empieza a regresar a su valor inicial durante el proceso de purgación, lo cual indica que las especies de NO<sub>2</sub> están dejando a la película de PANI. Mientras más alta la temperatura de calentamiento, mayor será la energía de activación para la desorción, y consecuentemente más rápida será la velocidad de desorción. Resultados similares también se han obtenido con el proceso de adsorción-desorción de moléculas de NH<sub>3</sub> en el mismo polímero.

**Descriptores:** Películas delgadas de polianilina; proceso de desorción de NO<sub>2</sub>; energía de activación para desorción; sensores optoquímicos.

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## 1. Introduction

Polyaniline (PANI) is a semiconductor polymer that has proven to be a good candidate for NO<sub>2</sub> [1-4] and other gas sensor applications [5-10]. The main interest in this material is that each of its redox states is related to a different electronic structure. A redox reaction between a chemical compound and PANI could result in a color change in this material, and the optical kinetics of a PANI film during a chemical sensing process describes the adsorption or desorption process of the absorbate species on the polymeric material. By using this particular property, the semiconducting PANI (emeraldine salt, ES, green color) has been used to detect low concentration NO<sub>2</sub> as well as NH<sub>3</sub> gas flux in a nulling optical-transmittance bridge system at room temperature in air [4,9]. Because of their strong electron acceptor behavior, NO<sub>2</sub> molecules tend to gain electrons when they interact with a more electronegative substance such as the green PANI and result in absorbed NO<sub>2</sub><sup>-</sup> species on the oxidized polymer [10]. The latter can be the sky blue or dark blue emeraldine base

(EB) depending on the NO<sub>2</sub> gas concentration: a relatively low concentration of NO<sub>2</sub> (<10 ppm) leaves a PANI film with a sky blue color (less oxidized), whereas an NO<sub>2</sub> gas of 30 ppm or higher causes a dark blue film (more oxidized). On the other hand, the interaction between NH<sub>3</sub> molecules and the ES PANI causes the proton transfer from this to NH<sub>3</sub> and forms adsorbed NH<sub>4</sub><sup>+</sup> species on the oxidized EB PANI film. The result of the NH<sub>3</sub> adsorption on PANI is also a color change observed in that material: from green to sky blue.

Although the absorption of both NH<sub>3</sub> and NO<sub>2</sub> on PANI causes the color change of the films from green to blue, the tone of the blue color is different in each case; namely the grade of oxidation differs from one to the other, which influences the desorption process of the adsorbates on PANI samples. For example, for the same gas concentration, the interaction of NH<sub>3</sub> with PANI leads to a much lower optical transmittance change than NO<sub>2</sub> [10]. After that, the NH<sub>3</sub> adsorbed PANI samples recovered their optical signal during the purging process with a dried N<sub>2</sub> gas flux at room temper-

ature (20°C), which could take 30 minutes or more. But an NO<sub>2</sub> absorbed PANI sample cannot recover its original optical properties under the same conditions, regardless of the gas concentration. Only the presence of ambient humidity could cause a partial desorption of NO<sub>2</sub> from PANI samples. This suggests that the interaction between NO<sub>2</sub> and PANI results in a strong chemical absorption of the toxic molecules on the polymeric material.

As a highly redox gas sensitive material, the adsorption-desorption response of a PANI film is a function of the film thickness. Thicker PANI film takes a longer time to reach the equilibrium value due to the permeable characteristics of polymer materials and the slower diffusion process of the adsorbates during the adsorption/desorption process. Some conducting polymer based sensors used ultra-thin films as sensing elements to get a fast response [1,2,11]. For example, the response time of three-layer (about 20 nm thick) PANI ultra-thin film prepared by the Langmuir-Blodgett (LB) technique to 20 ppm NO<sub>2</sub> was about 10 seconds, and it increased with the increase of the number of film layers [1]. On the other hand, a chemically deposited PANI film of 200 nm thick showed a 70% response time that was in the order of minutes for the same concentration of NO<sub>2</sub> [4]. From the technological point of view, however, the solution deposition method for thin film deposition is a cost-effective technique in comparison with LB ones for ultra-thin film preparation. The response speed of PANI thin film could be increased by reducing the film thickness and/or modifying its morphology in order to reduce the diffusion process in the polymeric film, or by heating the sensing element (PANI film) at a moderate temperature during the test. In the literature it is observed that the 70% response time of a spin-coated PANI composite film to 500 ppm NH<sub>3</sub> gas was 11 min when the testing temperature was 30°C, and it was reduced to 4 min when the measured temperature was 50°C [12]. The film thickness was not mentioned in the paper, but by considering the film preparation method (spin-coating) and its good mechanical properties as well as its slow response time, it should be more than 1 μm. Based on our previous works [4,9,10,13], it is found that the main concern of our optochemical sensor was the slow recovery of the optical signal in dried N<sub>2</sub> gas after PANI exposure to NO<sub>2</sub> and NH<sub>3</sub> gases. We report in this work that by heating the NO<sub>2</sub> or NH<sub>3</sub> absorbed PANI samples the desorption process of NO<sub>2</sub> from PANI samples can be accelerated. The kinetics of desorption is also discussed for both cases.

## 2. Experimental

Semiconducting ES PANI was obtained as thin films of about 200 nm thick on polycarbonate sheets (1.5 mm thick) by immersing these in an acidic (2M HCl) aniline solution at 3-5°C with 0.1 M NH<sub>4</sub>S<sub>2</sub>O<sub>8</sub> as the oxidant [14]. The Optical sensing system was the same as that reported above, using a 635 nm diode as the light source [4], with the exception that the PANI sample holder was replaced by a new one which was fitted

with a home-made heating element. Then the temperature of the PANI samples could be varied between room temperature (20°C) and about 100°C. The electrical circuit diagram of the temperature control element is shown in Fig. 1. The variable resistance (Preset in Fig. 1) is used to adjust the applied voltage and control the sample temperature. This voltage is sent to a differential amplifier, and at the same time the sample temperature is measured by a solid state temperature sensor (LM35) with a sensibility of 10 mV/°C. The voltage of the sensor is subtracted from the control one. If the difference is positive, it suggests that the sample temperature is lower than that of the settled one and a positive voltage is introduced in the output of the differential amplifier and, this, in turn, will set the current source in operation by sending a current ( $i$ ) to the resistance heating element. If the difference is negative, then the output of the differential amplifier will be a negative voltage, indicating that the sample temperature is higher than that of the control. In this case the current source will not be activated, leaving the sample to cool in air to the settled temperature.

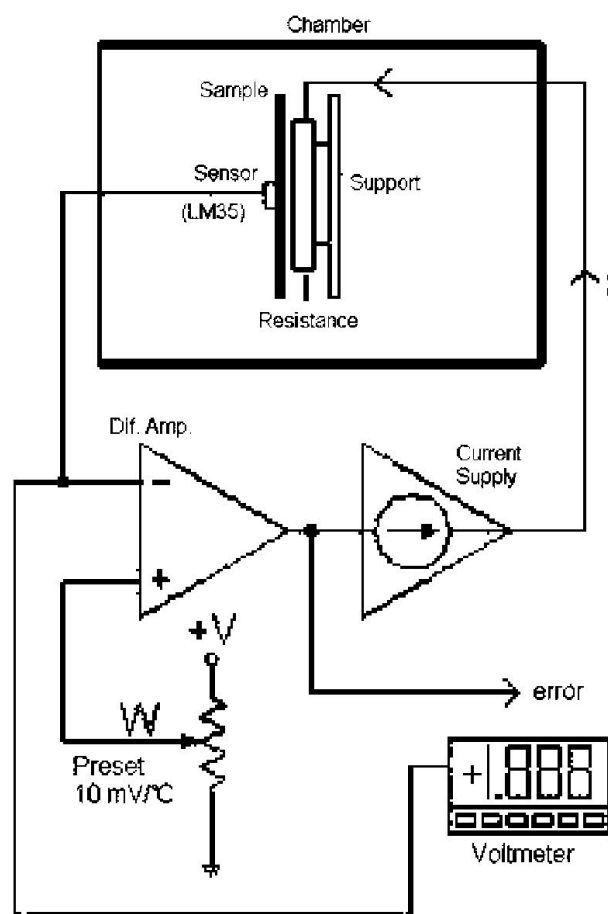


FIGURE 1. Diagram of the temperature control unit used for sample heating. The PANI thin film sample (Sample), located inside the gas test chamber (Chamber), is settled near a heating element (Resistance), whose temperature can be elevated by applying an electrical current ( $i$ ).

A PANI coated polycarbonate sheet with an area of about 2 cm × 2.4 cm was placed on the sample holder of the test chamber. Before the gas sensing test, a quartz sample was inserted onto the optical way of the system to give a calibrated optical transmittance change of about 4.5–6.5% at 635 nm, and then withdrawn. The NO<sub>2</sub> gas flux diluted in the dried N<sub>2</sub> was introduced into the chamber. The gas concentration was varied from 5 to 50 ppm, considering that it is a useful range for industrial applications such as HNO<sub>3</sub> production. After about 15 min of absorption, the NO<sub>2</sub> entrance was cut off, and a pure, dried N<sub>2</sub> gas was circulated inside the chamber to purge the toxic gas from the PANI sample. The temperature of this sample was chosen between 20 and 90°C during the purging process, considering the possible deprotonation of ES PANI samples at temperatures higher than 90°C [15]. 1000 ppm NH<sub>3</sub> gas was also used to test the thermal assisted desorption process in PANI films under the same conditions. Ex-situ optical absorbance spectra of PANI samples before and after NO<sub>2</sub> gas absorption-desorption process were recorded on a Shimadzu Spectrophotometer Model 3101 PC.

### 3. Results and discussion

When PANI thin film samples were in contact with NO<sub>2</sub> gas of a different concentration, their optical transmittance signals at 635 nm started to increase, as shown in Fig. 2. The color of the PANI sensing material changed from green to blue, due to the NO<sub>2</sub> molecule absorption, and it is quite logical to observe in the same figure that the magnitude of the optical transmittance change ( $\Delta T$ ) is proportional to the gas concentration. The response time of the sensing system for 20 ppm NO<sub>2</sub> gas was about 12 min to reach 70% of the equilibrium value. As soon as the testing gas was cut off and a

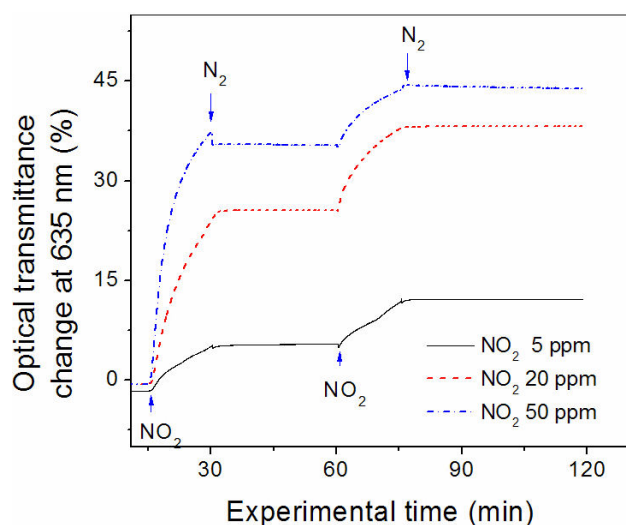


FIGURE 2. Optical transmittance changes of three PANI samples during NO<sub>2</sub> gas adsorption-desorption process under atmospheric pressure at room temperature. The gas concentration varied from 5 to 50 ppm. Purging gas: dried N<sub>2</sub> flux.

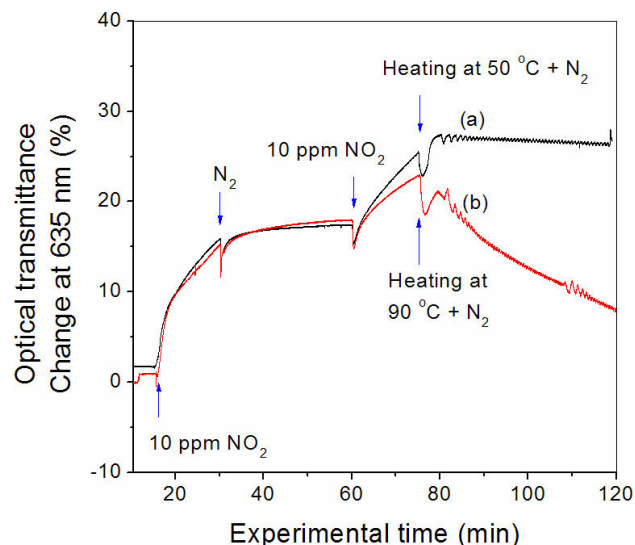


FIGURE 3. Optical transmittance changes of two PANI samples during the 10 ppm NO<sub>2</sub> gas adsorption-desorption process. In the final desorption process (80–120 minutes) the PANI samples were heated at (a) 50°C and (b) 90°C. Purging gas: dried N<sub>2</sub> flux.

purging gas (dried N<sub>2</sub>) was introduced into the test chamber, the increase in  $\Delta T$  stopped and its last value was maintained during the purging process for all the PANI samples kept at room temperature. This means that the introduction of the dried N<sub>2</sub> gas only interrupted the NO<sub>2</sub> absorption process on PANI samples and did not purge out any already absorbed NO<sub>2</sub> molecules from them. Further introduction of NO<sub>2</sub> gas renewed the absorption process, and the same unrecoverable optical transmittance phenomenon was observed again during the subsequent purging process.

Figure 3 shows the kinetic optical transmittance changes at 635 nm of two PANI samples at different sample temperature during the purging process to visualize the effect of thermal energy on the NO<sub>2</sub> desorption process. Initially the test chamber was filled with a 10 ppm NO<sub>2</sub> gas which causes the increase of the optical transmittance in PANI samples. After about 10 minutes of NO<sub>2</sub> gas circulation, this was cut off and the dried N<sub>2</sub> flux was introduced into the chamber to purge the test gas by keeping the PANI samples at room temperature. As expected, the change in the optical transmittance signals of the PANI samples was small enough to be considered negligible by taking into account the high sensitivity of the optochemical system [4]. Toxic gas with the same concentration was re-introduced into the test chamber for another 10 min, causing again an increase in the optical transmittance of the polymeric samples. At the end of adsorption process, the switch of heating element on the PANI sample holder was turned on and the polymeric samples were heated to 50°C (curve *a* in Fig. 3) or 90°C (curve *b* in Fig. 3). Now the optical transmittance signals began to decrease and the speed of this decrease increased with the sample temperature. The recovery time was about 80 min at 90°C under dried N<sub>2</sub> ambient (asymptotic extension of curve *b* to its intersection with Experimental Time axis in Fig. 3) in comparison with

an almost infinite time (Fig. 2) for recovery at 20°C. More adsorption-desorption cycles could be produced with an additional cooling system around the heating element to accelerate the cooling process, which is under construction. Finally, the small oscillation in the optical signal observed during the heating process comes from the polycarbonate (PC) substrates; it was shown that the same oscillation of the optical transmittance was observed by heating the PC sheets at 50 or 90°C in the chamber without PANI coating or testing gas.

The explanation of the recovery of the optical signal during the purging process should come from the NO<sub>2</sub><sup>-</sup> species desorption from the PANI samples. But before making such a claim, it is important to consider that the original PANI samples (ES, green) could lose dopant molecules (HCl) and result in the deprotonated ones (EB, blue) at temperatures higher than or equal to 90°C in air, as reported in the previous work [15]. However, the deprotonation of the ES PANI should lead to an increase in its optical transmittance at 635 nm (from green to blue), instead of a decrease observed in Fig. 3 during the purging process. As the optical signal of heated ES PANI at 90°C remained unchanged in the absence of any gas flux inside the test chamber (not showed here), it suggests that the heating process did not cause the deprotonation of ES PANI samples in this case and the recovery of the optical transmittance signal in the purging process with heating (Fig. 3) should indicate the desorption of the NO<sub>2</sub><sup>-</sup> species from the PANI samples. We observed that the minimum temperature required to initiate a kinetically observable NO<sub>2</sub> desorption process in oxidized PANI samples was equal to or higher than 50°C. Considering the chemical stability of semiconductor PANI samples, the heating temperature had settled at 90°C, at which the fastest desorption speed had been obtained for this polymer. Similar desorption behavior was also observed for PANI samples sensing NO<sub>2</sub> gas of a higher concentration such as 20 and 50 ppm. The higher the gas concentration, the more irreversible absorption is observed in PANI samples.

Other evidence of the NO<sub>2</sub><sup>-</sup> desorption from the PANI samples due to the heating process is observed in their ex-situ UV-VIS spectra. Figure 4a shows that for a 10 ppm NO<sub>2</sub> absorbed PANI sample, the N<sub>2</sub> purging process at room temperature did not restore the original optical spectrum of the polymer sample; the intensity of the broad absorption peak centered around 860 nm was slightly reduced after the gas absorption and not recovered after 6 days of the test. The same happened with a desorption temperature at 50°C (Fig. 4b), which suggests that up to that temperature the amount of the desorbed NO<sub>2</sub><sup>-</sup> species was not sufficient to lead to a notable color recovery in PANI films. But when the PANI sample was heated to about 90°C during the purging process, the optical spectra of the PANI sample before and after NO<sub>2</sub> absorption are similar (Fig. 4c), with the exception of a very small shift in the absorption peak. This indicates the effectiveness of the NO<sub>2</sub><sup>-</sup> specie desorption from the heated PANI films.

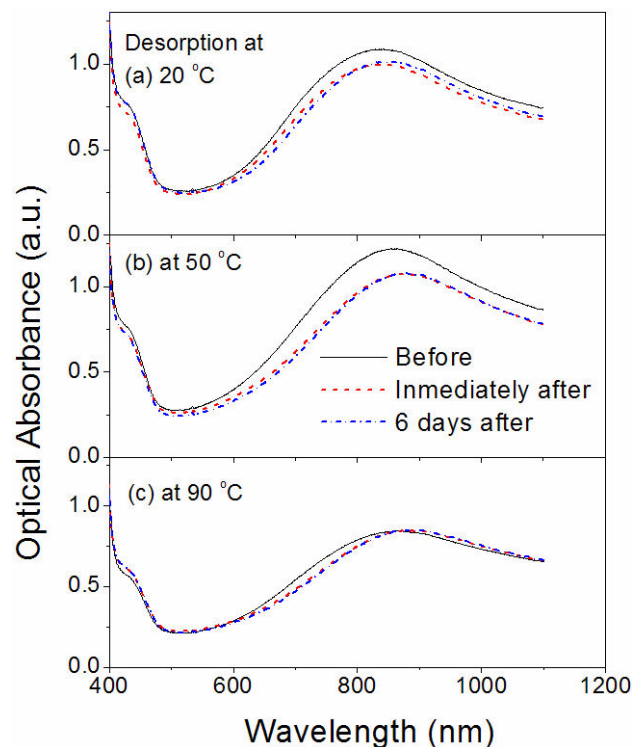


FIGURE 4. UV-VIS spectra of PANI samples before and after 10 ppm NO<sub>2</sub> absorption-desorption tests: (a) without, (b) with heating at 50 °C, and (c) with heating at 90°C during the final desorption process.

The NO<sub>2</sub> desorption curves in PANI thin film samples can be fitted by using the following equation [4,15]:

$$Y = Y_{\infty} + A_1 \exp(-t/\tau_{D1}) + A_2 \exp(-t/\tau_{D2}), \quad (1)$$

where  $Y$  is the optical transmittance change at time  $t$ ,  $Y_{\infty}$  the same parameter when  $t$  tends to infinity,  $A$  the weight factor and  $\tau_D$  the decay time of desorption process. The last one is related to the activation energy for desorption  $E_D$  in the following way:

$$\tau_D = \nu^{-1} \exp(E_D/kT). \quad (2)$$

Here  $\nu$  is the molecular vibration frequency (about  $10^{12}$  to  $10^{13}$  s<sup>-1</sup>),  $k$  the Boltzmann constant and  $T$  the absolute temperature of the sensing sample. The use of two terms of exponential decay for describing the desorption process of NO<sub>2</sub> molecules from PANI thin films originates from the two kinetically different desorption processes: the faster superficial desorption ( $\tau_{D1}$ ) and the slower volumetric diffusion-chemical reaction ( $\tau_{D2}$ , with  $\tau_{D2} > \tau_{D1}$ ). Figure 5 exhibits the fitting curves for (a) 10 ppm and (b) 20 ppm NO<sub>2</sub> gas desorption processes from PANI samples at 90°C. The activation energy values ( $E_D$ ) obtained from the decay times ( $\tau_D$ ) in fitting curves are listed in Table I. There are some interesting observations to be made. First, in the case of 10 ppm NO<sub>2</sub> desorption (Fig. 5a) the weight factor of the slower term is about 10 times larger than that of the faster one, suggesting that most of the absorbed NO<sub>2</sub> molecules were desorbed through the volumetric diffusion process. In the case

TABLE I. Activation energy for desorption ( $E_D$ ) of  $\text{NO}_2$  and  $\text{NH}_3$  molecules from PANI samples for different gas concentrations and at different desorption temperatures, calculated by using Eq.(1) with  $\tau_D$  as the decay time.

$\text{NO}_2$ desorption at $90^\circ\text{C}$			1000 ppm $\text{NH}_3$ desorption		
Gas (ppm)	$\tau_{D1}$ (s)	$E_{D1}$ (eV)	Temp ( $^\circ\text{C}$ )	$\tau_{D1}$ (s)	$E_{D1}$ (eV)
	$\tau_{D2}$ (s)	$E_{D2}$ (eV)		$\tau_{D2}$ (s)	$E_{D2}$ (eV)
10	5.13	0.91	20	0.70	0.68
	102.62	1.00		9.79	0.75
20	0.96	0.85	50	0.79	0.76
	32.70	0.96		20.50	0.85
50	1.28	0.86	90	1.59	0.87
	28.76	0.96		27.38	0.96

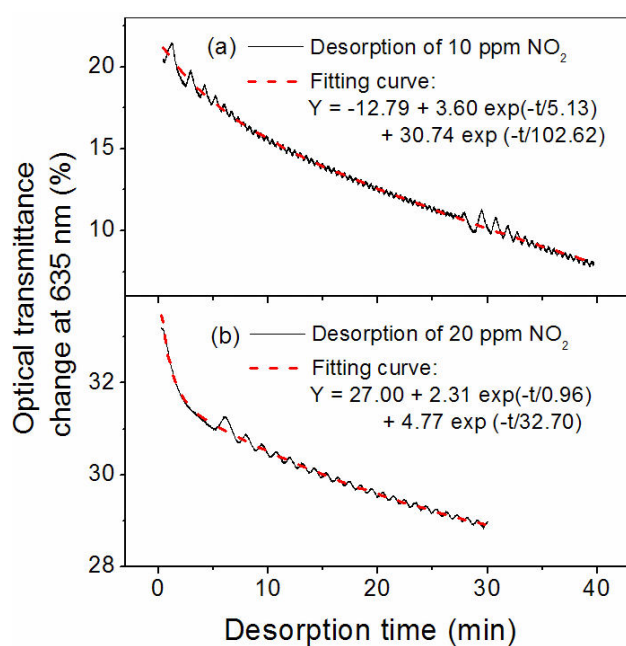


FIGURE 5. Fitting of  $90^\circ\text{C}$  desorption curves of PANI samples previously absorbed with (a) 10 ppm and (b) 20 ppm  $\text{NO}_2$  gas fluxes.

of 20 ppm  $\text{NO}_2$  absorption (Fig. 5b), however, this ratio is reduced to about 2:1, which means that with the increasing gas concentration, the percentage of superficial absorbed  $\text{NO}_2$  species is increased considerably. Second, the decay times of the desorption process ( $\tau_{D1}$  and  $\tau_{D2}$ ) are longer in the 10 ppm case than in the 20 ppm one, implying a higher activation energy for the 10 ppm  $\text{NO}_2$  desorption process than for the 20 ppm one, as shown in Table I. But the higher the  $\text{NO}_2$  gas concentration, the greater the irreversible absorption of  $\text{NO}_2$  molecules in PANI, which is reflected in the values of  $Y_\infty$  shown in Fig. 5. In the case of 10 ppm, a negative value of  $Y_\infty$  means that at some point in the experimental time (around 160 min in the curve Fig. 3b) the optical signal will go back to zero, meaning that the desorption will be completely reversible. On the other hand, a positive value of  $Y_\infty$  for 20 ppm  $\text{NO}_2$  gas implies that no matter how long the

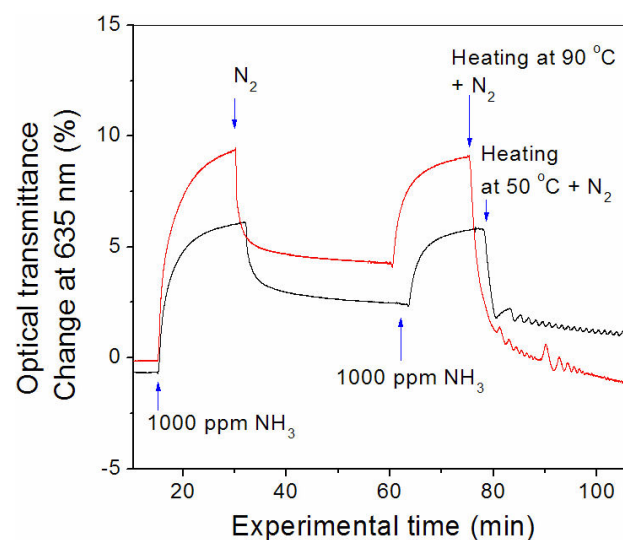


FIGURE 6. Optical transmittance changes of two PANI samples during the 1000 ppm  $\text{NH}_3$  gas adsorption-desorption process. In the final desorption process (80-120 minutes) the PANI samples were heated at 50 or  $90^\circ\text{C}$ . Purging gas: dried  $\text{N}_2$  flux.

experimental time, the optical transmittance change will never go back to zero. Therefore the complete color recovery for the 20 ppm  $\text{NO}_2$  absorbed PANI sample would not be possible. The same results were also obtained for 50 ppm  $\text{NO}_2$  absorbed PANI samples (Table I). The higher values of  $E_D$  in the 10 ppm  $\text{NO}_2$  absorbed PANI samples (0.91 ~1.0 eV, Table I), compared with those of the 20 and 50 ppm ones (0.85~0.96 eV, Table I), also indicate a thermodynamically more favorable desorption process in the former case.

The effect of PANI sample temperature was also observed for  $\text{NH}_3$  gas desorption kinetics. Figure 6 shows the optical transmittance change curves of two PANI samples in contact with a 1000 ppm  $\text{NH}_3$  gas flux. When the dried  $\text{N}_2$  was introduced into the test chamber to purge  $\text{NH}_3$ , the PANI sample heated at  $90^\circ\text{C}$  recovered 100% of its optical transmittance signal, whereas those at 20 and  $50^\circ\text{C}$  show a recovery of about 70% during the same interval of desorption time.

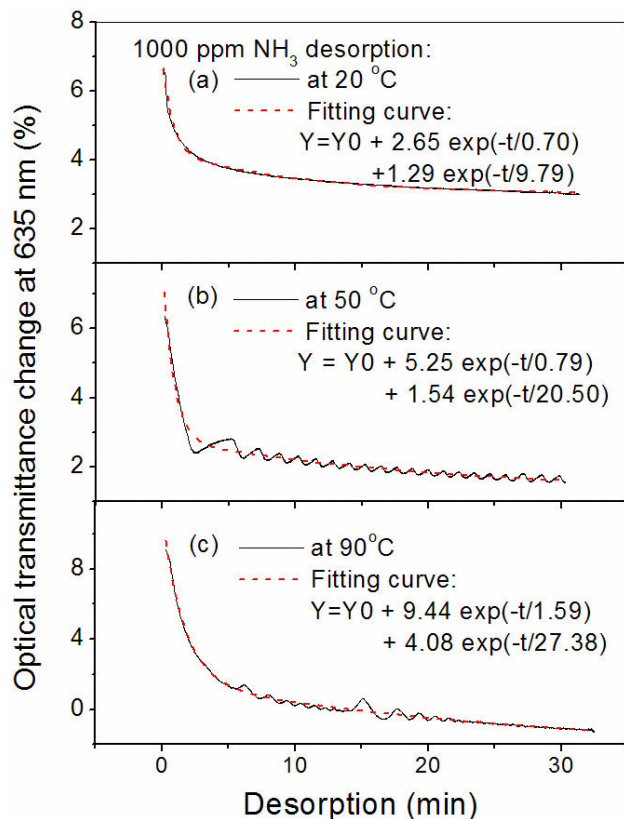


FIGURE 7. Fitting of desorption curves of PANI samples previous adsorbed with 1000 ppm NH<sub>3</sub> gas flux at (a) 20°C, (b) 50°C, and (c) 90°C.

A small lowering of the optical signal below the zero line observed in 90°C heated PANI sample in Fig. 6 after 100% recovery is an artifact of optical reference; the baseline of the optical system could be slightly shifted after testing and could be corrected by placing the quartz sheet and following the standard calibration procedure [9]. Figure 7 shows the fitting curves for the desorption process of PANI samples

at 20, 50 and 90°C. The higher the sample temperature, the higher the value of  $E_D$ , and consequently the more complete the desorption process occurring in the NH<sub>3</sub> adsorbed PANI samples. Finally it is worth mentioning that the PANI films used in this work were optically more absorbent than those reported in Refs. 9 and 15 due to the difference in the chemical bath temperature for PANI deposition. As a result the optical transmittance change for the same NH<sub>3</sub> gas concentration is greater and the desorption speed is slower in this work compared with those reported previously.

#### 4. Conclusions

It is observed in this work that the desorption kinetics of the strongly adsorbed NO<sub>2</sub> species from polyaniline (PANI) samples in a dried N<sub>2</sub> ambient is affected by the temperature of the polymer samples. At room temperature (20°C), the optical transmittance values ( $\Delta T$ ) of these PANI samples remain constant, implying a null desorption during the purging process. At temperatures higher than or equal to 50°C, a recovery of  $\Delta T$  begins to appear, and the desorption process reaches a notable speed at a sample temperature of about 90°C. In this case the optical signal of the PANI samples at about 635 nm could be totally reversible after sensing a 10 ppm NO<sub>2</sub> gas with an activation energy for desorption  $E_D$  of 0.9-1.0 eV. The same phenomenon is also observed in NH<sub>3</sub> adsorbed PANI samples.  $E_D$  in this case changes with the sample temperature from 0.68-0.75 eV at 20°C to 0.87-0.96 eV at 90°C.

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- D. Xie *et al.*, *Sens. Actuators B, Chem* **81** (2002) 158.
- N.E. Agbor, J.P. Cresswell, M.C. Petty, and A.P. Monkman, *Sens. Actuators B, Chem* **41** (1997) 137.
- P.S. Barker, A.P. Monkman, M.C. Petty, and R. Pride, *IEE Proc.-Circuits Devices Syst.* 144 (1997) 11.
- J. Elizalde-Torres, Hailin Hu, and A. García-Valenzuela, *Sens. Actuators B, Chem* **98** (2004) 218.
- P.N. Bartlett and S.K. Ling-Chung, *Sensors and Actuators* **20** (1989) 287.
- M. Hirata and L. Sun, *Sensors and Actuators* **40** (1994) 159.
- S. Unde, J. Ganu, and S. Radhakrishnan, *Adv.Mater.Opt.Electron.* **6** (1996) 151.
- K. Ogura, T. Saino, M. Nakayama, and H. Shiigi, *J.Mater.Chem.* **7** (1997) 2363.
- M.E. Nicho *et al.*, *Sens. Actuators B, Chem* **76** (2001) 18.
- J.Elizalde-Torres, Hailin Hu, and J.M.Saniger, *Rev. Mex. Fís.* **51** (2005) 482.
- M.K. Ram, O. Yavuz, and M. Aldissi, *Synthetic Metals* **151** (2005) 77.
- M. Matsuguchi, J. Io, G. Sugiyama, and Y. Sakai, *Synthetic Metals* **128** (2002) 15.
- H. Hu, M. Trejo, M.E. Nicho, J.M. Saniger, and A. García-Valenzuela, *Sens. Actuators B: Chem* **82** (2002) 14.
- L. Hechavarría, H. Hu and M.E.Rincón, *Thin Solid Films* **441** (2003) 56.
- H. Hu, J. Cadenas, J.M. Saniger, and P.K.Nair, *Polymer International* **45** (1998) 262.