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Ammonia absorption study of pulsed-plasma polyaniline by quartz crystal microgravimetry and UV/vis spectrometry

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ABSTRACT

The ammonia absorption properties of polyaniline elaborated by the pulsed-plasma technique are studied. These properties depend on the structure of the polymer which is associated not only to plasma parameters such as peak power, ignition and extinction durations, pulse frequency and duty cycle, but also to the type of doping agent. Two methods of analysis are used: the UV/vis spectrometry and the quartz crystal microbalance. The results show that input power is the most influent plasma parameter on the sensitivity of the polyaniline film. Moreover, the oxidative doping is more efficient than the acidic one to create more polarons and then to obtain a more sensitive layer. The gravimetric study shows that the interaction between ammonia molecules and iodine-doped polyaniline corresponds to a multilayer reversible chemisorption.

1. Introduction

The interests of electronic conducting polymers have been demonstrated in a large number of applications [1–4]. For the application in gas detection, electronic conducting polymers present numerous advantages compared to inorganic materials mostly used in commercial systems. Indeed, their advantages are principally not only their sensitivity at room temperature but also, their diversity, their easy synthesis and chemical stability. Among all conducting polymers, polyaniline (PANi) has shown the best properties for gas (ammonia) detection [5]. Polyaniline used as gas sensitive layer is generally synthesized by chemical or electrochemical routes and is associated to electrical or optical transducer [6–23]. The gas sensitive form of PANi, named polyemeraldine salt (conductive form), contains radical-cations $\overset{+\bullet}{\mathrm{N}}\mathrm{H}$ (polarons) which constitute the gas absorption sites. This conductive form is obtained by oxidative or acidic doping leading to the creation of radical-cations. The interaction of ammonia gas with doped PANi results in the change of the PANi doping state: the polaron density inside the band gap of the polymer decreases [5]. Consequently, electrical and optical properties of PANi are modified. In this work, we have elaborated polyaniline by an original, clean and dry method: the plasma technique, for the detection of ammonia. Moreover, plasma polymerization is a simpler synthesis process than conventional methods since fewer fabrication steps are necessary. To the best of our knowledge, our group has shown for the first time the possibility to use PANi sensitive layer elaborated by the plasma technique to realize an ammonia optical sensor [24].

The aim of this work is to study the influence of the structure of the plasma polymer on its ammonia absorption properties and then to understand the mechanisms of plasma PANi/NH_3 interaction. The structure of the pulsed-plasma PANi depends on the plasma parameters such as the input power, the ignition and extinction durations, the frequency of the pulse and the duty cycle. Moreover, this structure is also dependent on the doping method: acidic one by hydrochlorhydric acid (HCl) or oxidative one by iodine (I_2). The ammonia sensitivity has been studied by two methods: an optical one using UV/vis spectrometry and a gravimetric one by quartz crystal microbalance (QCM).

2. Experimental

2.1. Elaboration of pulsed-plasma polyaniline layers

Films were deposited in a cylindrical aluminum capacitively coupled pulsed-plasma reactor. The reactor consisted of two parallel circular electrodes (diameter 30 cm and thickness 1 cm) with a gap between them of 5 cm. The substrates (glass or Si/SiO_2 wafer) were placed on the lower polarized-electrode. A primary pump (Alcatel) and a turbomolecular pump (Alcatel) were used to attempt a 5×10^{-6} Torr ultimate pressure in the chamber. Then, the

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monomer vapour was introduced into the reactor from a glass container with aniline liquid maintained at room temperature (20 °C). The monomer vapour pressure into the reactor during the polymerization was maintained at 0.02 Torr using a throttle valve. The reactor pressure was measured using a Pirani gauge. The pulsed-plasma discharge was sustained by a radio-frequency (13.56 MHz) generator (Advanced Energy, Cesar 133) using a manual matching network. Peak power (P) was varied between 10 and 100 W, pulse on-time (t_{on}) and pulse off-time (t_{off}) between 2.5 and 90 ms, frequency (f) between 1 Hz and 30 kHz and duty cycle (*d.c.*) (defined as the ratio of pulse on-time to period) between 10 and 50%.

To minimize possible contamination from previous deposition, the reactor was cleaned regularly by 10 min consecutive oxygen and argon-plasma: RF-power—100 W; pressure—0.01 Torr; flows of O_2 or Ar—20 sccm. The flow rate of the gases (O_2 and Ar) was controlled by MKS gas flow meters (Type 1259C). The flow meters and the throttle valve were controlled by a central PC.

2.2. Doping process of pulsed-plasma polyaniline layers

To obtain a NH_3 sensitive thin film, it is necessary to dope polyaniline. Two types of dopants have been used: hydrochloric acid 37% (HCl, Aldrich) and iodine (I_2, Aldrich). In this work, the *ex situ* (out of the plasma reactor) doping method has been used. This method consisted in introducing PANi layer into a chamber saturated with iodine or hydrochlorhydric vapours during 48 h.

2.3. Physico-chemical characterizations of pulsed-plasma PANi films

The PANi films deposited onto Si/SiO_2 substrates have been analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were acquired with an ESCA LHS 12 instrument (Leybold) at the Laboratoire de Physique des Couches Minces (Institut des Matériaux de Nantes, France). The photoemission was excited by a monochromatic Mg Kα beam at 1253.6 eV. The emission was analyzed at a take-off angle of 90° relative to the sample surface, yielding a sampling depth around 10 nm due to the mean free path of the electrons [25]. Calibration was conducted on the C 1s peak of the C–C and C–H bonds at 285 eV. The binding energies were reliable to ±0.1 eV. The curve fitting was performed using CasaXPS software (Casa Software Ltd.). The peak shape was chosen with Gaussian (70%)/Lorentzian (30%) curve fitting. The elemental quantification was reliable to ±5%.

The PANi films deposited onto glass substrates have also been analyzed by UV/vis spectroscopy. The UV/vis spectra have been recorded thanks to a Cary 100 spectrophotometer (Varian). Windows-based Cary software was used for data acquisition and analysis.

In order to estimate the swelling of the polymer after doping, thickness measurements have been realized on plasma polyaniline deposited on Si/SiO_2 substrates, thanks to Dektak 8 apparatus (Veeco).

2.4. Optical sensing system

The optical sensor is made of pulsed-plasma PANi film deposited onto glass substrate as described above, and placed into the measuring chamber. The optical ammonia gas sensing system has already been described in previous publication [26]. It consists of a Cary 100 spectrophotometer in which the sealed measuring chamber has been inserted, a gas dilution system with flowmeters and a computer for data collection and analysis. At the beginning of the experiment, the zero point of spectrometer was carried out without the PANi sensor.

Nitrogen gas (99.99%, Air Liquide) was used as dilution gas. The flows of ammonia and nitrogen gases were precisely controlled by two flowmeters, which were plugged in a mass flow controller (MFC). A stream of nitrogen gas containing ammonia was passed through the polyaniline gas sensor and spectroscopic measurements were performed. The concentration of NH_3 gas in the measuring chamber was varied by mixing different flows of NH_3 gas and 500 sccm of N_2 gas. The concentration of NH_3 (ppm) was defined as the ratio of the flow rate of NH_3 gas to the total flow rate of NH_3 and N_2 gases. In this work, the ammonia concentration varied between 92 and 4618 ppm. The ammonia concentrations lower than 92 ppm were not measured due to experimental set-up limitation. After inserting the PANi sensor inside the measuring chamber, a certain amount of dried ammonia gas, diluted in nitrogen gas, was introduced into the measuring chamber. The interaction between NH_3 gas and the PANi film leads to optical absorbance variation of PANi. When the optical absorbance variation tends to a constant value depending on time, the NH_3 gas introduction was turned off and stream of pure N_2 gas was passed through the sensor to purge completely the NH_3 molecules in the measuring chamber and to regenerate the polyaniline sensor.

Sensitivity (S) was calculated as $(A - A_0)/A_0$ ratio, where A_0 is the initial optical absorbance of the sensor under N_2 and A the absorbance of the sensor when exposed to ammonia gas. The wavelength of the light source used in this work was fixed at 430 nm. All experiments were performed at room temperature.

2.5. Quartz crystal microbalance set-up

The set-up was based on a quartz resonator (AT-cut quartz, 14 mm, 6 MHz) running with a Maxtek TM-400 controller and placed in a 0.5 L chamber [27]. The sensitivity and accuracy of such technique are known to be very good: 10 pg cm^{-2} and less than ppm, respectively [28]. The chamber was vacuumed by a pumping system (Alcatel Drytel 1025) composed of a membrane pump and a turbomolecular one allowing to attempt a limit pressure less than 10^{-1} Pa. The ammonia vapour pressure, controlled by an automatic needle valve, could vary between vacuum up to 1.2 bar with an accuracy of around 2 mbar. This set-up enables to acquire the static mass uptake to build a mass isotherm representing the mass uptake as a function of ammonia pressure or to acquire a dynamic mass uptake representing the mass uptake as a function of time due to a sudden pressure increase. PANi thin film samples have been deposited in the middle of commercial quartz, as discs of 8 mm in diameter, and then doped.

3. Results and discussion

3.1. Influence of the type of doping agent on PANi absorption properties

In a first time, a bare quartz crystal and undoped PANi-plasma layer have been tested by QCM. The results show that, at 1000 mbar of NH_3, the absorbed ammonia mass is 0.13 μg/cm^2 for the bare crystal and 1.09 μg/cm^2 for the undoped PANi layer. So we can consider that the mass absorbed by the quartz crystal is negligible whereas that absorbed by undoped PANi layer is due to the presence of some absorption sites (radical-cations) created, before the doping process, during plasma polymerization as shown by XPS (Fig. 2a).

The influence of the type of dopant (HCl or I_2) is shown in Figs. 1 and 5a. Fig. 1 shows the mass uptake of NH_3 acquired by QCM by a PANi film doped with vapours of I_2 or HCl. The mass uptake is more important for the layer doped with iodine than with hydrochlorhydric vapours. Indeed, at 1090 mbar of NH_3,

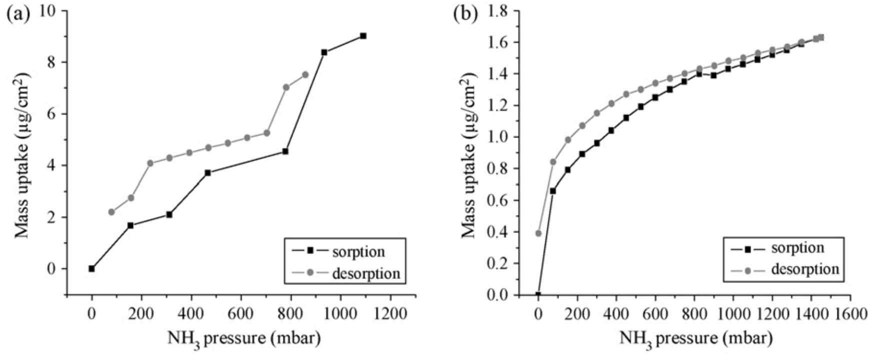

Fig. 1. Mass uptake as a function of NH_3 pressure for pulsed-plasma PANi layer (0.02 Torr, 10 W, 50%, 50 Hz) doped with (a) I_2 or (b) HCl. The lines between the experimental points are drawn only to guide the eye.

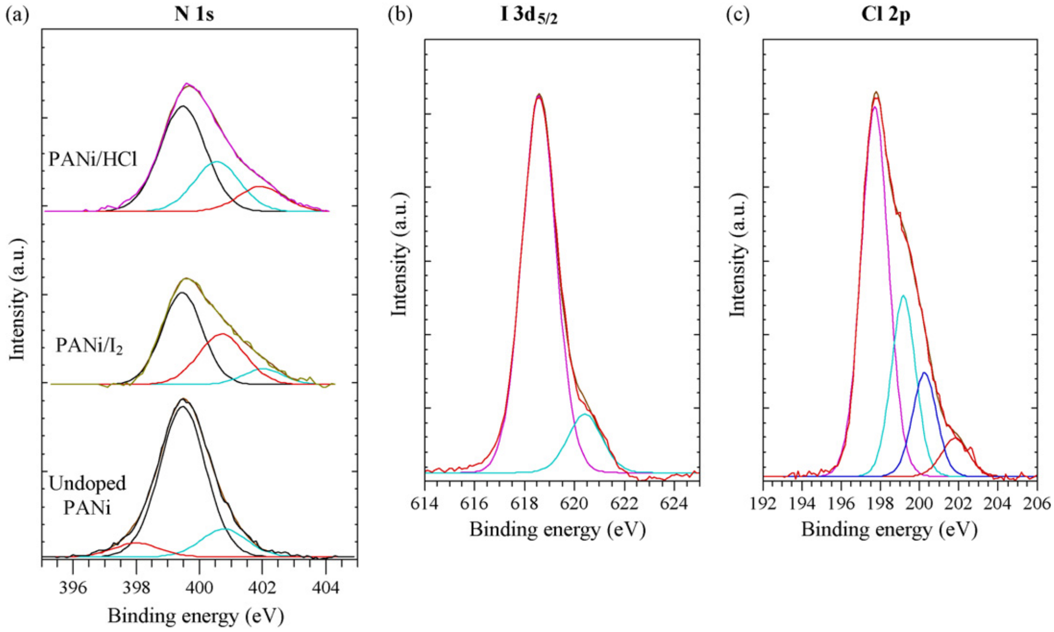

Fig. 2. (a) N 1s XPS core-level spectra of pulsed-plasma PANi films undoped, doped with I_2 or doped with HCl (0.02 Torr, 20 W, 80%, 80 Hz); (b) I $3d_{5/2}$ XPS core-level spectrum of PANi layer doped with I_2 (0.02 Torr, 10 W, 50%, 30 kHz); (c) Cl 2p XPS core-level spectrum of PANi layer doped with HCl (0.02 Torr, 10 W, 50%, 30 kHz).

the absorbed ammonia mass is 9.02 $\mu g/cm^2$ for the layer doped with I_2 and 1.47 $\mu g/cm^2$ for the layer doped with HCl. This result is confirmed by the sensitivity obtained by UV/vis spectrometry for pulsed-plasma PANi layers synthesized at different discharge powers (Fig. 5a). In order to explain this result, pulsed-plasma PANi films have been analyzed by XPS and UV–vis spectrometry. Table 1 presents the XPS ratio of doping agent on total nitrogen for different conditions of polymer synthesis. This ratio is in general more important for the oxidative doping meaning that iodine doping is more efficient than acidic one. Moreover, Fig. 2a shows N 1s XPS spectra of pulsed-plasma PANi films undoped, doped with I_2 or doped with HCl. The N 1s peak of the undoped layer can be fitted with three components at 398.3, 399.5 and 400.8 eV assigned to imine (–N=) species, amine (–NH–) groups and positively charged nitrogen ($N^{+(\bullet)}$), respectively. The undoped form is composed principally of amine groups. After doping, the imine species have disappeared, the intensity of the amine groups has decreased: this decrease is more important for the oxidative doping, and a new peak appears at 402 eV attributed also to positively charged nitrogen ($N^{+(\bullet)}$). The –NH–/$N^{+(\bullet)}$ ratio comes from 4.75 for the undoped PANi layer to 1.4 for the HCl-doped layer and 1.2 for the I_2-doped layer. Then, two doping sites are available: the amine groups and the imine groups. It seems that I_2 molecules have more affinity for the amine groups than HCl molecules. It is confirmed by the doping of PANi layers that do not contain imine species (synthesized at 10 W, 50% and 30 kHz) [29] where oxidative doping leads to I/N ratio equal to 0.5 and acidic doping to Cl/N ratio equal to only 0.1 (Table 1).

Table 1
Dopant/N ratio of PANi films elaborated in different plasma conditions and doped during 48 h with I_2 or HCl vapours (XPS data).

Conditions of synthesis (*P*, *d.c.*, *f*)	I/N	Cl/N
20 W/10%/100 Hz	0.6 ± 0.06	0.4 ± 0.04
20 W/30%/100 Hz	0.3 ± 0.03	0.3 ± 0.03
20 W/80%/80 Hz (t_{on} = 10 ms, t_{off} = 2.5 ms)	0.4 ± 0.04	0.3 ± 0.03
20 W/10%/10 Hz (t_{on} = 10 ms, t_{off} = 90 ms)	0.4 ± 0.04	–
10 W/50%/30 kHz	0.5 ± 0.05	0.1 ± 0.01

Another explanation for the best sensitivity of I_2-doped films is provided by the decomposition of dopant XPS spectra. The core-level spectrum of I $3d_{5/2}$ (Fig. 2b) can be decomposed into two components lying at 618.6 and 620.4 eV. According to many authors [30–33], these two peaks can be attributed to ionic iodine, corresponding respectively to I_3^- and I_5^- ions, then directly associated to doping. The Cl core-level spectrum (Fig. 2c) presents a doublet corresponding to Cl $2p_{3/2}$ and Cl $2p_{1/2}$ that can be fitted with two spin-orbit-split doublets. The main doublet with the Cl $2p_{3/2}$ peak lying at 197.7 eV corresponds to ionic species, Cl^- acting then as dopant by the formation of N^+Cl^- bounds. The doublet with the Cl $2p_{3/2}$ peak lying at 200.3 eV can be assigned to covalent species [34]. These covalent species can be due either to trapped HCl molecules that have not reacted or to C–Cl bounds formed by addition of HCl molecules on polymer chain double bonds. Indeed, double bonds are created during plasma polymerization by aromatic ring openings leading to the formation of aliphatic acyclic chain containing double bonds. In conclusion, contrary to iodine, chlorine atoms in the PANi polymer do not act all as doping agents.

Finally, the UV/vis spectra of undoped plasma PANi, doped with I_2 or HCl are very different (Fig. 3). Indeed, the undoped PANi film presents just one peak at 260 nm. The iodine-doped PANi presents two peaks at 294 and 367 nm with a shoulder at 260 nm whereas the spectrum of the chlorine-doped PANi is formed of a peak at 260 nm and just a shoulder at around 400 nm. The UV/vis spectrum of emeraldine salt (doped chemical PANi) shows three absorption bands: the π–π^* transition of conjugated ring systems at 330 nm, the π–polaron transition at 430 nm and the polaron–π^* transition at 800 nm [35]. Then we can attribute the absorption bands of iodine-doped plasma PANi to the π–π^* transition at 260 nm, the π–polaron transition at 294 nm and the polaron–π^* transition at 367 nm. Compared to chemical PANi, the absorption bands are shifted to shorter wavelength certainly due to shorter conjugated chains. The absorption bands of HCl-doped PANi can be assigned to the π–π^* transition at 260 nm and the shoulder at around 400 nm to polaron–π^* transition. As the intensity of the bands associated to polarons is very less important for PANi-HCl, we can conclude that less polaron are created by acidic doping.

Fig. 1 shows also hysteresis between the sorption and the desorption curves, meaning that the interaction between ammonia molecules and absorption sites created by doping corresponds to a reversible chemisorption. Moreover, the sorption curve of I_2-doped PANi presents three steps (at 100, 300 and 900 mbar) whereas just one appears on the PANi-HCl curve. In order to explain this result, a kinetic study has been done on the PANi-I_2 layer until 0.6 mbar of NH_3 (Fig. 4). This figure shows that the absorption rate is the same for each step meaning that the steps are not due to different absorption sites. So we can attribute these steps to a multilayer absorption. Ammonia molecules first react with surface absorption sites (1st step) and then diffuse in the layer (plateau) releasing then the surface absorption sites then available for other ammonia molecules, and so on until no more polaron are available. As less polarons are created during acidic doping, they may be present just on the surface of the PANi film explaining then the presence of just one step.

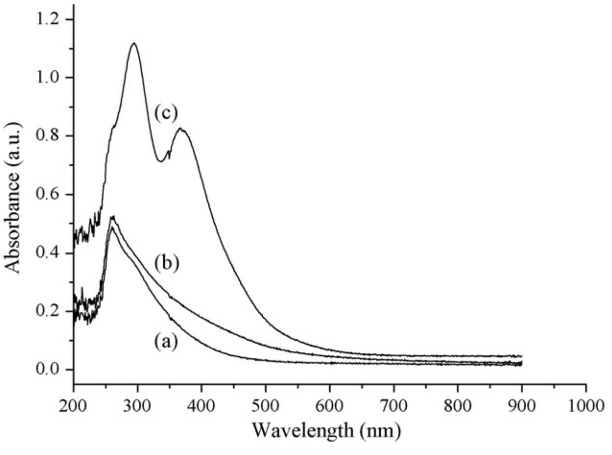

Fig. 3. UV/visible spectra of pulsed-plasma PANi (0.02 Torr, 20 W, 10%, 10 Hz): (a) undoped, (b) doped with HCl or (c) doped with I_2.

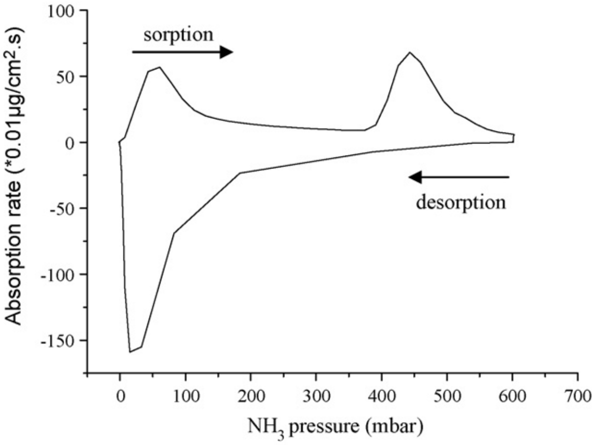

Fig. 4. Ammonia absorption rate as a function of ammonia pressure.

3.2. *Influence of the plasma parameters on PANi absorption properties*

3.2.1. *Discharge power*

The sensitivity of PANi-I_2 decreases rapidly when the discharge power increases and the layers elaborated at 50 and 100 W are not sensitive to ammonia (Fig. 5a). The sensitivity of PANi-HCl increases slightly between 10 and 20 W and then decreases: the layer elaborated at 100 W is not sensitive to ammonia. This result is confirmed by the QCM analysis showing that the mass uptake by PANi-I_2 elaborated from 10 to 50 W decreases (Fig. 5b). These results can be associated to the swelling of the polymer after doping. There is a direct link between the swelling of the polymer due to doping and the sensitivity of the film. When the discharge power used to elaborate the PANi layer increases, the polymer swelling after I_2 doping decreases (Fig. 5c). Then the doping becomes less efficient by increasing the power. Indeed, we have shown that the increase of the discharge power leads to the increase of the PANi cross-linking and to the decrease of the quantity of nitrogen [29]. A highly cross-linked polymer is little accessible as well for I_2 molecules than for ammonia ones; and less nitrogen means less doping sites and then polarons. Concerning the acidic doping, the swelling increases between 10 and 20 W and then decreases. The increase of the synthesis power induces more imine species with which HCl molecules react preferentially [29], explaining then the increase of the swelling after HCl doping and the sensitivity to NH_3 between 10 and 20 W. However, at 50 W, the important cross-linking prevents HCl and NH_3 molecules to attain doping sites or absorption sites.

3.2.2. *Ignition and extinction durations of the plasma phase*

When the on-time varies between 2.5 and 40 ms ($t_{off} = 10$ ms) or when the off-time varies between 2.5 and 90 ms ($t_{on} = 10$ ms), the mass uptake remains almost the same. Moreover, in these same conditions, the polymer swelling due to acidic or oxidative doping is constant. Then, for these values of on-time and off-time, the film sensitivity does not seem to depend on off- or on-times. Moreover, the I/N ratio remains constant when off-times vary (Table 1).

3.2.3. *Frequency*

The sensitivity to ammonia and the mass uptake remain the same until around 100 Hz and then increase with the frequency until 30 kHz (Fig. 6a and b). When the frequency increases, the

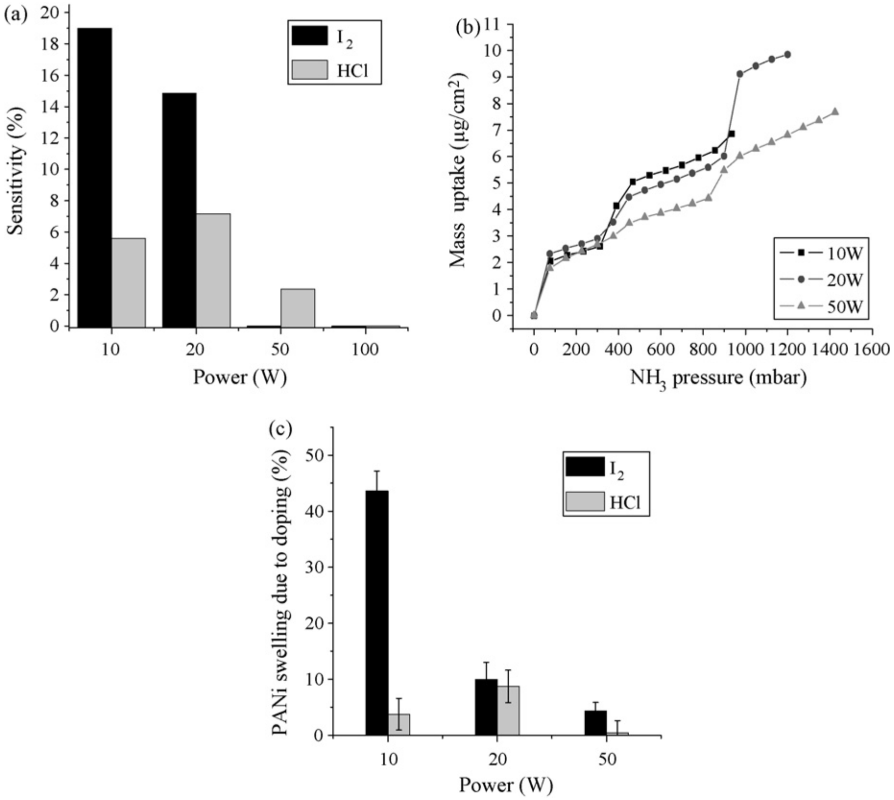

Fig. 5. (a) Sensitivity at 3230 ppm of NH_3 of pulsed-plasma PANi layers elaborated at different discharge powers (0.02 Torr, 10%, 100 Hz) and doped by I_2 or HCl; (b) mass uptake as a function of NH_3 pressure of pulsed-plasma PANi layers elaborated at different discharge powers (0.02 Torr, 50%, 30 kHz) and doped by I_2; (c) swelling of pulsed-plasma PANi layers elaborated at different discharge powers (0.02 Torr, 50%, 50 Hz) after doping by I_2 or HCl.

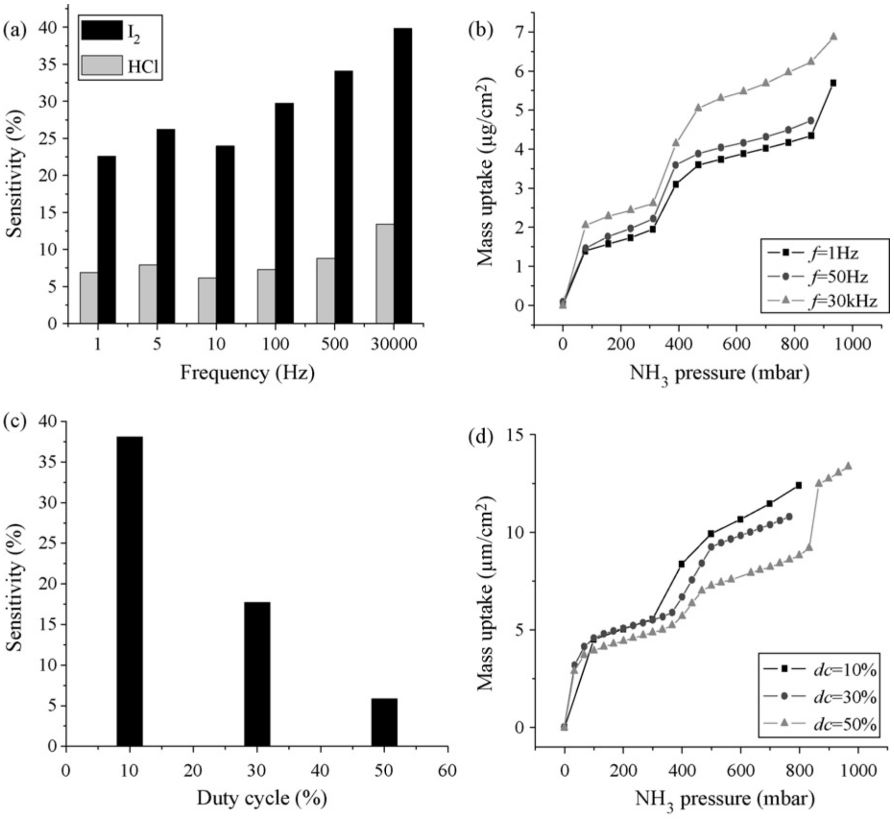

Fig. 6. (a) Sensitivity at 3230 ppm of NH_3 of pulsed-plasma PANi layers elaborated at different frequencies (0.02 Torr, 10 W, 50%) and doped by I_2 or HCl; (b) mass uptake as a function of NH_3 pressure of pulsed-plasma PANi layers elaborated at different frequencies (0.02 Torr, 10 W, 50%) and doped by I_2; (c) sensitivity at 3230 ppm of NH_3 of pulsed-plasma PANi layers elaborated at different duty cycles (0.02 Torr, 20 W, 100 Hz) and doped by I_2; (d) mass uptake as a function of NH_3 pressure of pulsed-plasma PANi layers elaborated at different duty cycles (0.02 Torr, 20 W, 100 Hz) and doped by I_2.

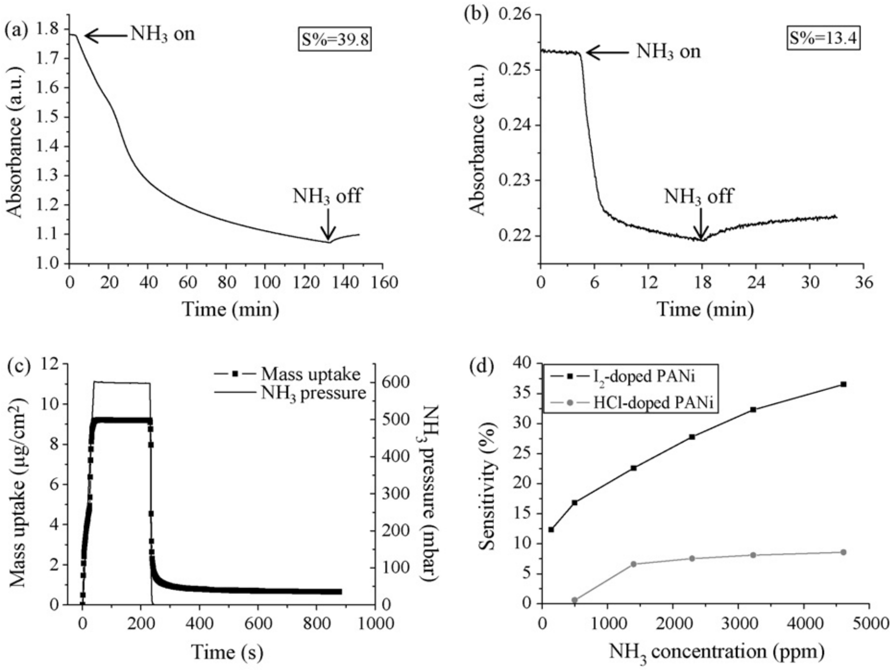

Fig. 7. (a and b) Dynamic optical response (λ = 430 nm, [NH$_3$] = 3230 ppm) of a PANi layer (0.02 Torr, 10 W, 50%, 30 kHz) doped by I$_2$ (a) or HCl (b); (c) dynamic gravimetric response ($p_{NH_3} = 600$ mbar) of pulsed-plasma PANi layer doped by I$_2$ (0.02 Torr, 20 W, 30%, 100 Hz); (d) sensitivity of pulsed-plasma PANi layer (0.02 Torr, 10 W, 50%, 30 kHz) doped by I$_2$ or HCl as a function of ammonia concentration.

on-time and the off-time decrease. At 100 Hz, the on-time is equal to 5 ms (*d.c.* = 50%). So, it seems that the on-time has an influence on the sensitivity when it is lower to 5 ms (between 5 and 0.017 ms which correspond to *f* = 30 kHz).

When the on-time decreases, our previous studies have shown that the ring opening and cross-linking decrease [29]. Then, ammonia molecules can attain more easily the absorption sites. Then, the best sensing results have been obtained at high frequency (low t_{on}) when the layer is the most ordered with the higher quantity of iodine (Table 1): I/N ratio increases with the frequency.

3.2.4. Duty cycle

Fig. 6c and d shows that when the duty cycle increases, the sensitivity and the mass uptake decrease. The increase of the duty cycle corresponds to the increase of on-time and then of cross-linking of PANi layer, as well as to a decrease of I/N ratio (Table 1). Moreover, the swelling of the polymer due to doping is less important at high duty cycle, meaning that the doping is less efficient when the PANi layer is elaborated at high duty cycle, leading then to the creation of less polaron available for ammonia absorption.

3.3. Performance of the ammonia sensor

The kinetics of the optical response to 3230 ppm of NH$_3$ of a PANi layer doped by iodine or HCl vapours are plotted in Fig. 7 a and b, respectively. When the ammonia gas is injected into the measuring cell, the deprotonation process of the plasma PANi occurs leading to a decrease of the absorbance at 430 nm. When the equilibrium between the absorbed ammonia molecules in PANi film and in gas phase is obtained, no more variation of the absorbance is observed. Finally, when the injection of ammonia is turned off, the ammonia molecule desorption (protonation) begins to restore the equilibrium of the concentrations and as a result, the absorbance of the sensor increases. The response time appears to be higher for the layer doped by I$_2$. Indeed, the response time is 2 h and 18 min for the layer doped by I$_2$ and HCl, respectively. Moreover, the regeneration of the sensor corresponding to NH$_3$ desorption is slowly reversible. However, QCM allows obtaining fast response and recovery times as shown in Fig. 7c. This graph represents the mass uptake by I$_2$-doped PANi to a sudden ammonia pressure increase (600 mbar) and shows the immediate response of the plasma polymer and its fast regeneration when ammonia is turned off, i.e. when the chamber is vacuumed again. Notice that the remaining mass uptake corresponds to a remaining NH$_3$ pressure (some mbars) due to the fact that another pump (less efficient) has been used to vacuum NH$_3$. A further efficient pumping allows recovering the initial pressure. That shows that the sorption is fully reversible. Another way to improve the gas desorption process consists to heat PANi layer [36] or to expose it again to doping agents such as hydrochloric acid at room temperature [10].

Moreover, our studies have shown a good repeatability of the responses. However, a decrease of the absorbed ammonia gas of around 50% is observed after 5 months on a same layer. It can be attributed to the ageing of the layer due certainly to the desorption of the iodine dopant.

In Fig. 7d, the sensitivity of the sensor as a function of ammonia concentration is illustrated. The sensitivity increases with increasing ammonia concentration and approaches a plateau value at around 1500 ppm of NH$_3$ for HCl-doped PANi and higher than 5000 ppm for I$_2$-doped PANi. The non-linear behavior of the response to ammonia gas was also observed for several PANi ammonia sensors [11,37]. This behavior can be explained by the gas diffusion phenomenon in the material and the saturation of the absorption sites.

4. Conclusion

We have shown in this study that pulsed-plasma technique is well-adapted to elaborate PANi films sensitive to ammonia. The most influent plasma parameter on the sensitivity of PANi is the discharge power. The most sensitive pulsed-plasma PANi layers have been obtained using a low discharge power and a low on-time (corresponding then to high pulse frequency and low duty cycle). In these conditions, the aromatic ring scission is low leading to linear structures rather than cross-linked polymers. Moreover, the oxidative doping is more efficient than the acidic one leading to the creation of more polarons which constitute the ammonia absorption sites. Indeed, the pulsed-plasma polyaniline is constituted principally by amine functions compared with imine ones and the amine groups react preferentially with I_2. The gravimetric study has shown that the interaction ammonia/PANi-I_2 corresponds to a multilayer reversible chemisorption. However, the response time of the PANi-I_2 film is higher than that of the PANi-HCl layer. However, our results show that piezoelectric transduction (QCM) seems interesting to obtain low response and regeneration times. Finally, the evolution of the swelling of the polymer after doping well represents the evolution of ammonia sensitivity of the polymer.

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