

Engineered doped and codoped polyaniline gas sensors synthesized in N,N-dimethylformamide media

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Abstract Conducting Polyaniline films (Pani) on Corning glass substrates, produced using either an in-situ doping process or a co-doping process, were prepared by the oxidative polymerization of aniline in N,N-dimethylformamide. Bicyclic aliphatic camphorsulfonic acid (CSA), aromatic toluenesulfonic acid (TSA) and carboxylic trifluoroacetic acid (TFA) were employed as doping agents, and CSA mixed with TSA and CSA mixed with TFA were employed as the co-doping materials. The topography of the Pani films was analyzed by atomic-force microscopy (AFM), and their doping and oxidizing states were characterized by Fourier-transform infrared (FT-IR) spectroscopy and optical (UV-Vis) spectroscopy. Flower-like clusters, microfibers, and nanofibers were obtained by doping with CSA, TSA, and

the mix of both (CSATSA), respectively. The flower-like morphology limits the conductivity of the film while the microfiber morphology leads to a highly conductive film. The conductivity of the films increases with the doping level, coil-like conformation of the chain and the protonation of the imine in quinoid units. The codoped process reduces the roughness of the CSA-doped films by 50%, but the conductivity depends on the acid type used for this process (TSA or TFA). The optical gas sensor response of the films is related to both the morphology and the degree of protonation. In this study, Pani with a microfiber morphology obtained from TSA-doping is the most sensitive to ammonia gas sensing, and Pani with flower-like morphology is the least sensitive.

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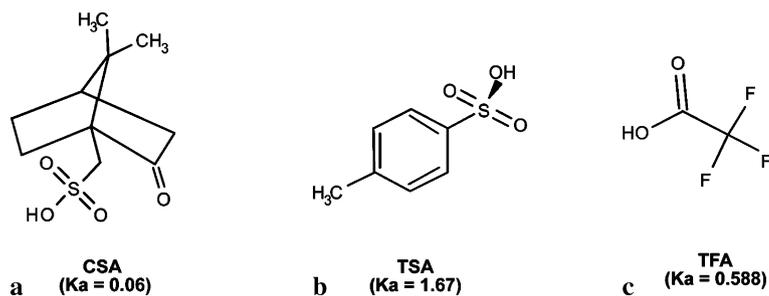
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1 Introduction

Polyaniline (Pani) has been widely used as an electrochromic material and as a sensing material [1–4]. The high sensitivity of Pani to the modification of its conductivity or optical properties by changes to its environment make it most promising for use in gas sensors; moreover, the chemical stability and especially the multiple oxidation states of Pani are attractive properties for use in gas sensors [1, 3]. If this polymer is fully reduced, it is called leucoemeraldine, which is formed of only benzenoid units and amine groups, contrary to the case if Pani is fully oxidized (Pernigraniline), which is composed of quinoid rings and imine groups. Emeraldine base (EB) is the half-oxidized state of nonconducting polyaniline. Emeraldine Salt (ES) is the half-oxidized state and protonated form of Pani, making it an intrinsically electrically conductive polymer. The protonation or doping process can be performed during the polymerization of the monomer in the presence of Brønsted acids [5–9]. Usually, strong hydrochloric (HCl) and camphorsulfonic (CSA)

Fig. 1 Chemical structures of the doping agents: (a) CSA, (b) TSA, (c) TFA



acids are the primary acids that are employed for the doping process. The use of each of these acids imparts particular properties on Pani. For example, HCl doped-Pani exhibits the highest electrical conductivity but also exhibits low solubility, which can be improved with a stabilizer [5]. CSA doped-Pani is slightly soluble, but it is less electrically conductive because of the chirality of the anion [10], and it tends to become de-doped in a short amount of time.

The low solubility of ES-Pani prevents the formation of electrically conductive thin films. To overcome this low solubility, a common solution is to synthesize Pani in the presence of acids and to subsequently mix it in an ammonia solution for at least 3 h to obtain EB-Pani (nonconductive), which is highly soluble in organic solvents, such as DMF and *m*-cresol [10–12]. The solution of EB-Pani in an organic solvent is casted or spin-coated onto substrates to form thin films. Subsequently, they are immersed or exposed in acids to induce electrical conductivity [11, 12]. Sometimes, EB-Pani powder is dissolved with the dopant to prepare the conductive films, but this process requires several days of stirring to obtain a homogeneous solution, and the homogeneous morphological structure of the films is not guaranteed [12]. However, several studies have focused on developing the aqueous system [1–6], with the objective of increasing the solubility of Pani and bypassing the organic system. In this study, to exploit the organic synthesis, conducting Pani thin films were obtained from in-situ doping (one acid) or co-doping (two acids) with different organic acids in an organic media of *N,N*,dimethylformamide (DMF). The influence of the type of doping agent and of the codoped process on the morphology and on the molecular structure was studied by AFM and FT-IR, respectively. The optical response of the films was measured during exposure to ammonia gas to evaluate its gas sensor response.

2 Experimental

Aniline monomer (99%, Aldrich) was distilled and stored at 5°C before use. (\pm)-10-Camphorsulfonic acid (CSA, 99%), *p*-toluenesulfonic acid (TSA, 98.5%), trifluoroacetic acid (TFA, 99%), ammonium peroxydisulfate (APS, 99.99%,

(NH_4)₂S₂O₈), *N,N*,dimethylformamide (DMF) and chloroform (CHCl₃) reagent grade were purchased from Sigma–Aldrich and were used as received.

The synthesis procedure is similar to that reported in the literature but with some important modifications [13]. Doped Pani films were prepared as follows. Aniline monomer (1.9 mmol) was mixed in 4 ml of DMF in a beaker and stirred for 30 min. Subsequently, one of the doping agents, as shown in Fig. 1 (CSA, TSA, or TFA), was added to the monomer solution, and stirring was maintained for 30 min to ensure the complete incorporation of the agent into the solution. Before they were added, CSA (2.9 mmol) and TSA (3.52 mmol) powders were dissolved in 5 ml of DMF. TFA liquid (64 mmol) was added directly into the solution. APS (0.45 g) dissolved in 5 ml of DMF was added slowly (10 drops/min) into the acid-monomer system (pH of approximately 1.9). Subsequently, 16 ml of chloroform was carefully added to the APS-acid-monomer system. After adding the chloroform, the pH of the solution was approximately 0.6. When the solution turns blue, four Corning™ glass substrates, which were previously cleaned, were vertically immersed into the beaker for 3 hours to obtain the Pani films on the glass substrates. Finally, the Pani-coated glass substrates were carefully removed, washed with DMF and dried at room temperature.

The codoped films were obtained as follows. A CSA-monomer solution was prepared with aniline (1.9 mmol) and CSA (2.9 mmol) following the steps described above. Subsequently, a second agent (3.52 mmol of TSA or 1.42 mmol of TFA) was mixed with the APS solution before mixing it into the CSA-monomer solution. Then chloroform (16 ml) was added, and when the solution turned blue, the Corning glass substrates were immersed into the beaker for 3 hours. Finally, the Pani-coated glass substrates were washed and dried at room temperature.

The thickness of the films was measured using a Dektak profilometer. The doped Pani films had thicknesses of 261 nm (CSA), 425 nm (TSA) and 342 nm (TFA). For the codoped Pani films, the thickness is approximately 329 nm for CSATSA and 350 nm for CSATFA.

The topography of the films was characterized by using a Nano Scope IV multimode scanning probe microscope

in tapping mode using a silicon tip under ambient conditions. The resistivity or conductivity ($\sigma = 1/\text{resistivity}$) of the films was measured by using the four-probe method with a Loresta GP MCP-T600 resistivity meter with software that calculates the resistivity correction factors by using a 4-pin probe at constant current (100 mA–0.1 mA). A probe of SPS-type for small samples, with an interpin distance of 1.5 mm, 0.26 R, and a spring pressure of 70 g/pin, was used. For the measurement, the thickness and dimensions of the film were input into the software, and the probe was directly placed onto the surface of the film to obtain the resistivity or conductivity values.

For the FT-IR measurement, Pani was compressed with KBr powder to obtain pellets, and the pellets were placed into a Bruker Vector 33 FT-IR spectrophotometer to acquire the infrared absorption spectra and examine the molecular structure of the doped and codoped Pani samples. UV-Vis spectroscopy of the films was performed in the wavelength range of 300–1100 nm using a Shimadzu 1601 PC spectrophotometer. A thermogravimetric analysis was performed using a Q500 V6.3 thermogravimetric analyzer at a heating rate of 10°C/min up to a temperature of 900°C in nitrogen atmosphere.

The dc-nulling optical transmittance was recorded in a closed system previously implemented to evaluate the chemical sensing response of the films [2]. A light-emitting diode (LED) at a wavelength of 630 nm was used as the light source. A flux of 83 ml/min of ammonia (NH₃) gas diluted (500 ppm) in dry N₂ gas was circulated during the experiment. All of the chemical sensing tests were performed at room temperature.

3 Results and discussion

The topography of doped and codoped Pani films supported on Corning glass substrates is displayed in Fig. 2. The 2D images over a 5 $\mu\text{m} \times 5 \mu\text{m}$ area show that the topography of the Pani films changes according to the nature of the dopant anion. Flower clusters of different lateral sizes and a height of approximately 1000 nm are observed in the dark green Pani films doped with a chiral CSA anion (see Fig. 2a). The TSA anion produces transparent green Pani films with a mixture of two morphologies: microfibers and polymeric islands (agglomerates). Well-defined grains with sizes of approximately 300 nm and with irregular tips projected perpendicularly to the surface (see 3D images not shown here) are observed in the green Pani doped with the TFA anion. This type of morphology is modified with the codoped process of the CSA-Pani with TSA or TFA (Figs. 2d and 2e). The CSATSA-doped Pani film exhibits similar morphology to the TSA-doped Pani film, but the microfibers and agglomerates are

smaller in size, and large agglomerates of irregular size are observed in the CSATFA-doped Pani film. The chemical structure of the doping agent and the co-doping process clearly influence the roughness (R_{ms}) of the Pani: CSA ($R_{\text{ms}} = 111 \text{ nm}$) > CSATFA ($R_{\text{ms}} = 52 \text{ nm}$) > TSA ($R_{\text{ms}} = 51 \text{ nm}$) > CSATSA ($R_{\text{ms}} = 36 \text{ nm}$) > TFA ($R_{\text{ms}} = 24 \text{ nm}$). A rougher film ($R_{\text{ms}} = 111 \text{ nm}$) is obtained from the sulfonate anion of CSA, and a smoother film ($R_{\text{ms}} = 24 \text{ nm}$) is obtained from the carboxylic anion of TFA. The surface roughness of the films is also modified with the addition of a secondary dopant, resulting in films almost 50% less rough than films without the addition (see Table 1).

The electrical conductivity is an important parameter of a conducting polymer (see Table 1). The average conductivity of 10^{-4} S/cm is measured for the Pani film doped with CSA, and the Pani film doped with TSA has a conductivity of 10^{-2} S/cm . A higher electrical conductivity of 0.1 S/cm is obtained for the flatter film (TFA-doped Pani). The rougher film (from the CSA anion) is three orders less conductive than the flatter and smoother film (from the TFA anion). In the first instance, an increase in the conductivity of the CSA-doped films could be expected via the codoped process. This increase depends on the type of the secondary dopant used; the aromatic acid (TSA) increases the conductivity three orders of magnitude, and TFA increases the conductivity only one order of magnitude. This difference could be ascribed to the K_{a} value of each acid (see Fig. 1) and related to the doping degree, or protonation, of the Pani film.

The oxidation state and protonation of the Pani films were measured in the FT-IR experiments (Fig. 3). Two peaks at 1556–1608 cm^{-1} and 1454–1523 cm^{-1} are associated with the oxidized state of Pani, and three main peaks at 1294–1299 cm^{-1} , 1230–1240 cm^{-1} and 1130–1165 cm^{-1} are attributed to the protonation of the doping process [5, 14–21]. In all spectra displayed in Fig. 3, the C=C stretching mode associated with the Benzenoid (1485–1496 cm^{-1}) and Quinoid (1571–1587 cm^{-1}) rings are well defined, indicative that the Pani films are composed of amine and imine units [14]. The shift of these bands can be attributed to the protonation of the Pani films [22]. The amount of quinoid (Q) and benzenoid (B) units indicates the oxidation state of the Pani film and could the level of oxidation can be estimated using the Q/B intensity ratio. This intensity ratio is in the range of 0.995 to 1.032 (see Table 1), suggesting a half-oxidized state (emeraldine) in the structure of the Pani films. It is worth mentioning that the slight difference in quinoid units could be due to the influence in the protonation of the imine groups. On the other hand, the band assigned to the in-plane bending vibration mode of C–H in N=Q=N, Q–N⁺H–B and B–N⁺H–B appears as a broad and strong band in the range of 1116 cm^{-1} to 1141 cm^{-1} . The presence of peaks at 1242–1257 cm^{-1} , related to the C–N⁺ or C=N⁺ stretching vibration in the polaron structure, confirms the doping of the Pani films. The intensity of this band

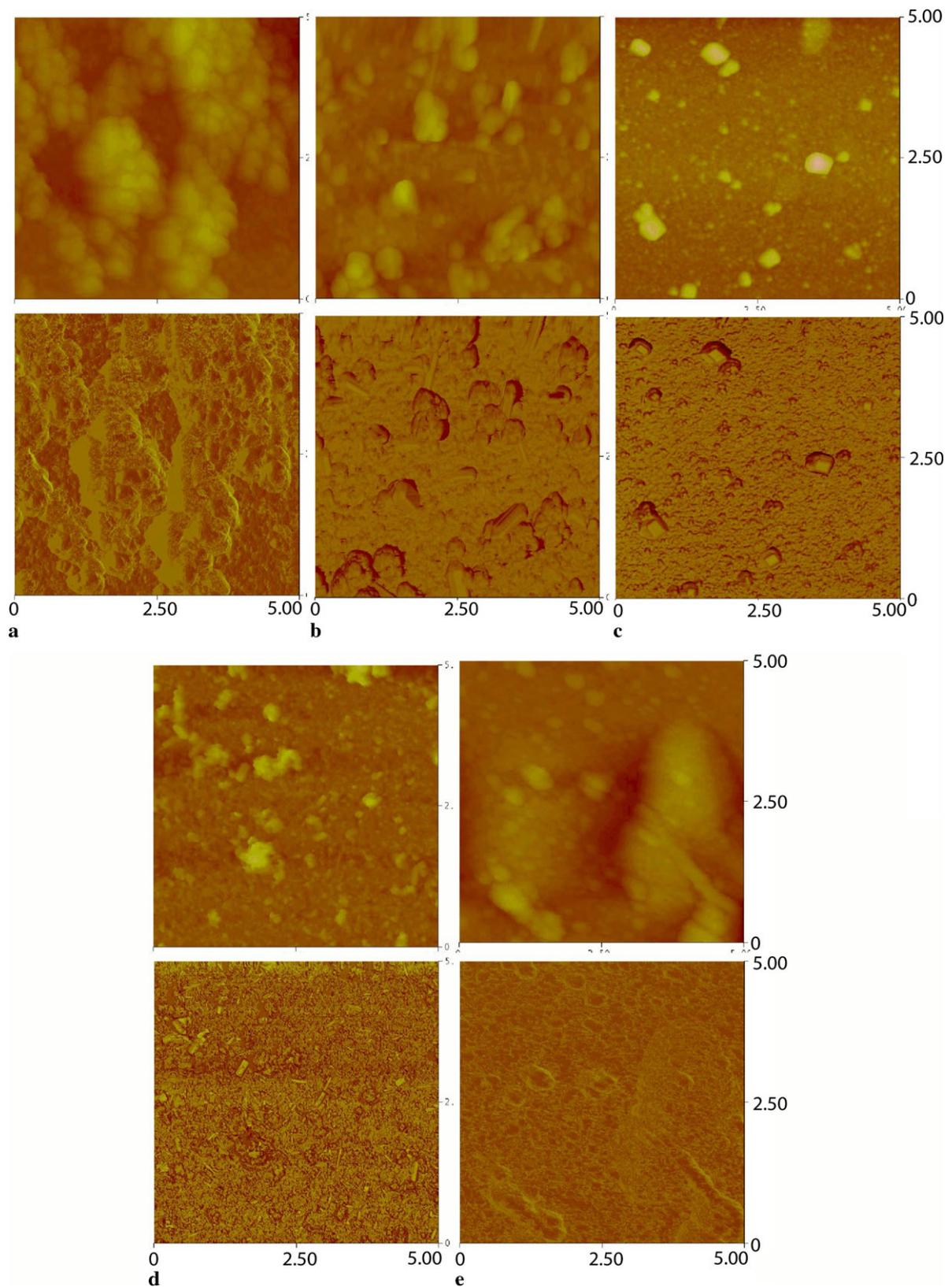


Fig. 2 AFM images of 2D of polyaniline films single doped with (a) CSA, (b) TSA, and (c) TFA and codoped with (d) CSATSA and (e) CSATFA. The scale is $5 \mu\text{m} \times 5 \mu\text{m}$

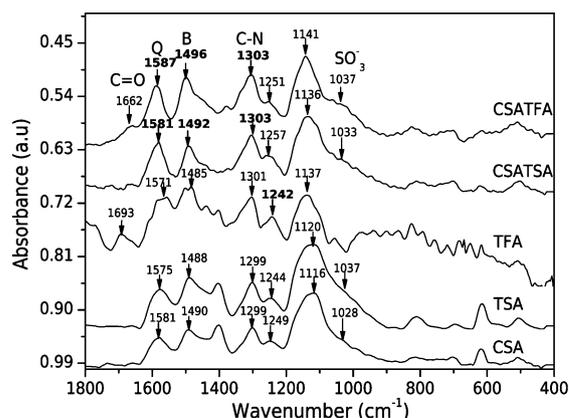
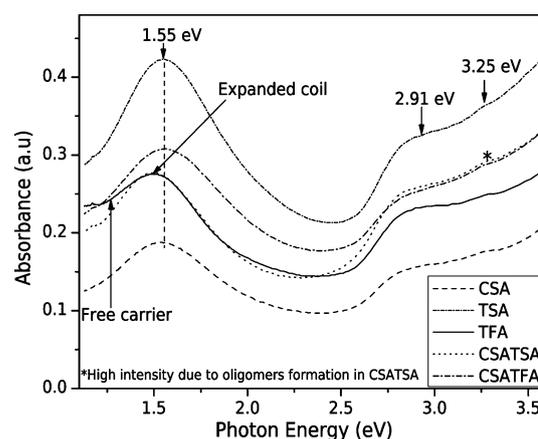
Table 1 Physical properties of conductive polyaniline films. Roughness (R_{ms}), conductivity (σ), polaronic and benzenoid (B) bands from UV-Vis spectra, doping level (DL) determined from the absorbance

Pani films	R_{ms} (nm)	σ (S/cm)	Q/B ratio from IR	Polaronic and B bands (nm)	DL	Temp. (°C)	Loss weight (%)
Flowers CSA	111	1E-4	1.01	809, 380	1.07	235, 285	17, 56, 10
Microfibers TSA	51	1E-2	1.03	800, 380	1.17	231, 291	17, 58, 9
Flat TFA	24	0.1	1.02	830, 380	1.11	223, 288	17, 54, 10
Nanofibers CSATSA	36	0.1	0.99	830, 380	0.96	220, 265	9, 38, 12
CSATFA	52	1E-3	1.0	794, 380	1.07	230, 270	14, 40, 18

 $A_{(\text{polaronic})}/A_{(\text{benzenoid})}$ intensity ratio and temperature of decomposition from TGA (Temp.)

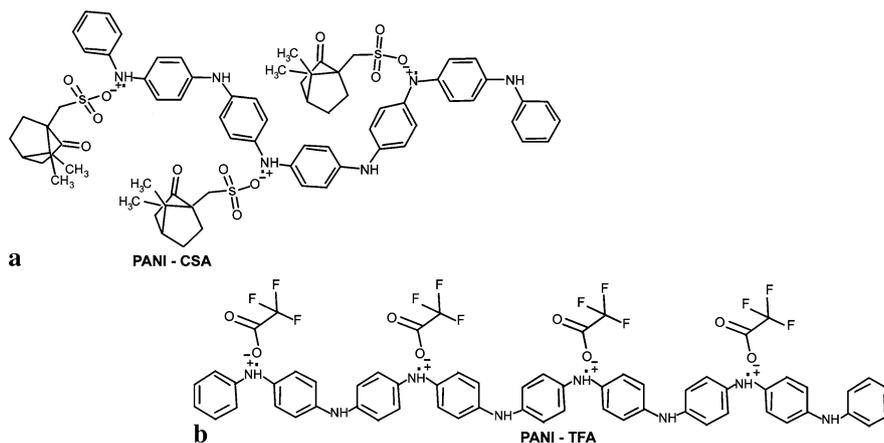
is related to the degree of doping level [12]. The highest intensity of this band is observed in the TFA-doped Pani film, demonstrating a high protonation of the Pani film. The band at $1299\text{--}1303\text{ cm}^{-1}$ is assigned to the C–N stretching mode of secondary (--N=) aromatic amine group for the benzenoid unit or π electron delocalization induced in the polymer by protonation. The absorption from the carboxylic (COO^-) anion of the TFA acid and the sulfonate (SO_3^-) of the CSA and TSA acids should appear at $1676\text{--}1700\text{ cm}^{-1}$ (C=O) and at $1031\text{--}1047\text{ cm}^{-1}$ (O=S=O and S–O symmetric and unsymmetrical stretching mode), respectively [5, 16–18]. In the TFA-doped Pani spectra, the C=O band appears at 1693 cm^{-1} , and the sulfonate band is observed as a broad peak at $1028\text{--}1037\text{ cm}^{-1}$ in the CSA- and TSA-doped Pani spectra. The slight shifting of these peaks is attributed to the acid used when doping the Pani films, and it could depend on the chemical structure of the acid and the electrostatic interactions with the main chain. The CSA- and TSA-doped Pani spectra show a sharp peak at 615 cm^{-1} , which could be attributed to the sulfonate group [22]. The blue-shift of the Benzenoid, Quinoid, and C–N bands in the CSATSA- and CSATFA-doped Pani spectra could be due to the presence of the secondary anion incorporated during the co-doping process.

The doped and codoped Pani films were analyzed using UV-Vis spectroscopy (Fig. 4). It is well known that non-conductive Pani (emeraldine base) presents two bands at 3.54 eV (350 nm) and 1.93 eV ($630\text{--}650\text{ nm}$) corresponding to the $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions of the benzenoid ring and the exciton absorption of the quinoid ring, respectively [19, 23]. The band at 1.93 eV disappears after the protonation process, and two new bands appear at 2.91 eV (425 nm) and at 1.6 eV (750 nm), which is indicative of a fully protonated Pani salt (conductive polymer) [5, 6]. The optical absorption spectra displayed in Fig. 4 show three bands at 3.25 eV , 2.91 eV and 1.55 eV as a result of the transitions of π to π^* , π to polaronic band, and polaronic band to π^* band, respectively. The first two peaks are unchanged in all spectra, but the position and width of the third band is susceptible to the type of anions used in this study. The third


Fig. 3 Infrared spectra of single doped (CSA, TSA, TFA) and codoped (CSATSA, CSATFA) polyaniline

Fig. 4 Optical absorbance in the visible range for single doped and codoped polyaniline films

band appears at 1.54 eV , 1.55 eV and 1.49 eV for Pani doped with the CSA, TSA and TFA anions, respectively. The broad peak shifted toward the infrared of TFA-doped Pani (from 1.55 eV to 1.49 eV) indicates an expanded coil conformation structure, leading to the formation of a free-carrier tail of a delocalized polaronic band, while the sharp band of the TSA-doped Pani is characteristic of a coil con-

Fig. 5 Coil and expanded coil conformations of single doped Pani with (a) CSA and (b) TFA, respectively



formation chain, which could affect the conductivity of the polymer. The codoped Pani (using CSATSA) also shows the same red-shift as the TFA-doped Pani, but with a small free-carrier tail, and the absence of this up-shift in CSATFA-doped Pani is characteristic of a coiling of the polymer chain. The doping level (DL) calculated from the intensity ratio of the polaronic (1.49–1.55 eV) and the $\pi-\pi^*$ bands (2.91 eV) is presented in Table 1. The doping level is in the range of 0.96 to 1.17, which is related to the electrical conductivity of the films. CSA and TSA contain the sulfonate group (SO_3^-), but CSA is a weaker acid than TSA. Therefore, less protonation is expected: 1.07 for doping with CSA and 1.17 for doping with TSA. These levels of protonation are consistent with the measured doping levels. In addition, these levels are also consistent with the Q/B intensity ratio observed in FT-IR spectra: 0.99 for doping with CSA and 1.03 for doping with TSA. These changes in Q/B ratio can be attributed to the presence of more quinoid units in TSA versus CSA, resulting in more imine groups that can be protonated. The difference of 0.1 in the doping level between these two samples increases the electrical conductivity by two orders of magnitude in TSA-doped Pani relative to CSA-doped Pani: 10^{-4} S/cm for CSA-doped Pani and 10^{-2} S/cm for TSA-doped Pani. In contrast, even though TFA (K_a approximately 0.588) is a weaker acid than TSA (K_a approximately 1.67), the TFA-doped Pani film shows higher conductivity than the TSA-doped Pani film. This result is not consistent with the doping level value, so it could be attributed to the expanded chain conformation, large free-carrier tail and flat morphology observed in the UV-Vis and the AFM results. In the case of codoped samples, CSATSA-doped Pani films show higher conductivity than CSATFA-doped Pani films, despite its lower doping level. The lower doping level can be explained by the content of oligomers formed in the films (high absorption at 380 nm marked as a star), but its high degree of conjugation helps the carrier charge transport [23], which could contribute to the electrical conductivity. On the other hand, the protonation should

increase with the addition of a secondary dopant in codoped Pani films. However, this increase did not occur for the CSATFA-doped film compared with TFA-doped film. In this case, the secondary dopant may protonate the amine group instead of the imine group, because the amine protonation does not provide new charge carriers unlike to the imine protonation [7]. This explanation is consistent with the Q/B ratio (1.0 for CSATFA and 1.02 for TFA) and with the doping level values (1.07 for CSATFA and 1.17 for TFA), as shown in Table 1.

The morphology, oxidation state, structural conformation, and doping level influence the electrical conductivity of the Pani films. Charge transport in the Pani films proceeds by an inter or intramolecular process, and it depends on the arrangement or alignment of the dopant with the polymeric chain (Fig. 5). The high conjugation caused by the steric repulsion between Pani molecules and TFA produces a flat surface morphology and an expanded coil conformation structure, along with a free-carrier tail in the FT-IR data, i.e., good alignment exists between the TFA and the Pani chains. In contrast, the chiral CSA anion interacting with Pani leads to a coil conformation chain and produces very rough films, leading to inhibited charge transport. However, the sulfonate anion from the aromatic TSA promotes good electrical and morphological properties in Pani as compared with the sulfonate anion from bicyclic aliphatic CSA.

The thermal stability of the doped and codoped Pani films was characterized by thermogravimetry measurements (Fig. 6). The thermograms (Fig. 6a) show three stages of thermal transitions leading to the observed weight losses. The first maximum weight loss occurs at about 220–230°C, which is attributed to the decomposition of the dopants and leads to de-doping of the polymer. The major weight loss at about 265–291°C is due to the dedoping process and the degradation of the polymer chain. At higher temperatures, the small weight loss may be due to the complete degradation of backbone units of polymer. The derivatives of the two main weight losses are shown in Fig. 6b; the degradation

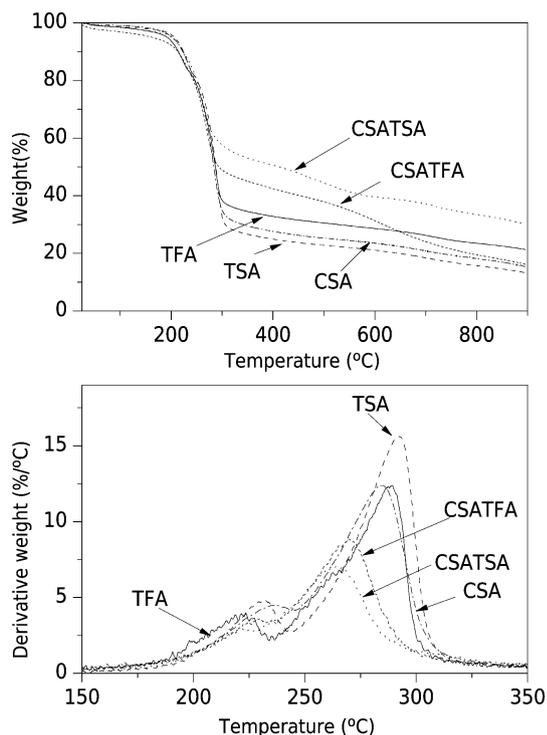


Fig. 6 TGA profiles of single doped and codoped Pani

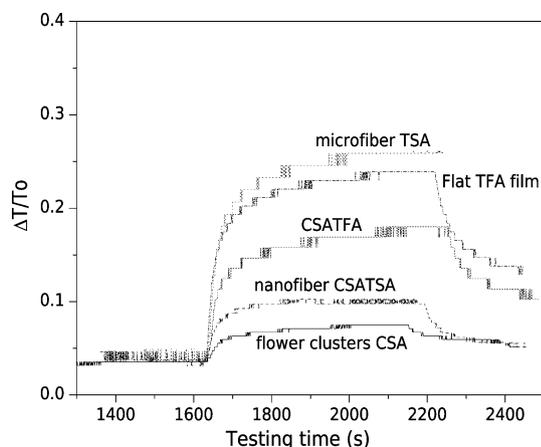


Fig. 7 Optical response of single doped and codoped polyaniline films in the presence of NH_3 gas

of the Pani clearly depends on the doping or codoping processes. The thermograms of the doped samples are shifted by almost 20°C at higher temperatures compared with the thermograms of the codoped samples, i.e., the doped samples are slightly more thermally stable.

Figure 7 shows the optical transmittance of the doped and codoped Pani films as a function of the exposure time in an ammonia atmosphere (flux of 83 ml/min @ 500 ppm) at room temperature. The adsorption of NH_3 clearly depends on the surface morphology of the doped and codoped Pani films. In the doped samples, the lowest transmittance

corresponds to the flower-like morphology of the CSA-doped Pani films, with the flat TFA-doped Pani films having higher transmittance, and the highest transmittance in the microfiber-morphology of the TSA-doped Pani films. This sequence corresponds to the doping level sequence observed in the UV-Vis data: 1.07 for CSA $<$ 1.11 for TFA $<$ 1.17 for TSA. Despite the presence of the sulfonate anion in the CSA- and TSA-doped Pani films, there are large optical differences resulting from a small difference in the doping levels. This difference could be due to the chemical structure of the tail—bicyclic aliphatic for CSA and aromatic for TSA—which could influence the NH_3 adsorption. For codoped samples, the sequence of the optical transmittance is nanofibers CSATSA (DL = 0.96) $<$ CSATFA (DL = 1.07). The relative intensity of the optical transmittance is correlated to the NH_3 adsorption. This adsorption is related to the de-doping of the Pani, i.e., de-protonation of the Pani with NH_3 to form an NH_4^+ anion. According to the figure, flower and nanofiber morphologies limit the adsorption of ammonia unlike the microfiber morphology and flat morphology; this difference could be due to the protonation level in the chain. The most sensitive film in this study is doped Pani using TSA.

4 Conclusions

Doped and codoped polyaniline films were successfully obtained from oxidative polymerization of aniline in organic media. The type and chemical structure of the doping agent primarily influence the morphology and conductivity of the films. Pani with morphologies consisting of flower clusters, microfibers, and nanofibers were obtained by doping with chiral CSA, aromatic TSA and a mixture of both, respectively. The codoping process of CSA-doped Pani films improves both the roughness and the gas sensing response of these films by almost twofold. The TSA-doped and TFA-doped Pani films are very promising for the development of gas sensor devices, so future studies will focus on them.

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References

- H. Hu, M. Trejo, M.E. Nicho, J.M. Saniger, A. García-Valenzuela, Adsorption kinetics of optochemical NH_3 gas sensing with semiconductor polyaniline films. *Sens. Actuators B* **82**, 14 (2002)
- J. Elizalde-Torres, H. Hu, A. García-Valenzuela, NO_2 -induced optical absorbance changes in semiconductor polyaniline thin films. *Sens. Actuators B* **98**, 218 (2004)

- H. Hu, B.E. Ortíz-Aguilar, L. Hechavarría, Effect of pH value of poly(ethylenimine)-H₂SO₄ electrolyte on electrochromic response of polyaniline thin films. *Opt. Mater.* **29**, 579 (2007)
- U. León-Silva, M.E. Nicho, H. Hu, R. Cruz-Silva, Effect of modified ITO substrate on electrochromic properties of polyaniline films. *Sol. Energy Mater. Sol. Cells* **91**, 1444 (2007)
- M.C. Arenas, E. Andablo, V.M. Castaño, Synthesis of conducting polyaniline nanofibers from single and binary dopant agents. *J. Nanosci. Nanotechnol.* **10**, 549 (2010)
- C. Arenas, G. Sánchez, Optical, electrical and morphological properties of transparent binary doped polyaniline thin films synthesized by in situ chemical bath deposition. *Polym. Int.* **60**, 1123 (2011)
- N.V. Blinova, J. Stejskal, M. Trchová, J. Prokes, Polyaniline prepared in solutions of phosphoric acid: Powders, thin films, and colloidal dispersions. *Polymer* **47**, 42 (2006)
- G. Anitha, E. Subramanian, Dopant induced specificity in sensor behaviour of conducting polyaniline materials with organic solvents. *Sens. Actuators B* **92**, 49 (2003)
- A. Rahy, T. Rguig, S.J. Cho, C.E. Bunker, D.J. Yang, Polar solvent soluble and hydrogen absorbing polyaniline nanofibers. *Synth. Met.* **161**, 280 (2011)
- M.M. Ayad, E.A. Zaki, Doping of polyaniline films with organic sulfonic acids in aqueous media and the effect of water on these doped films. *Eur. Polym. J.* **44**, 3741 (2008)
- E. Bormashenko, R. Pogreb, S. Sutovski, A. Shulzinger, A. Sheshnev, G. Izakson, A. Katzir, Infrared optics applications of thin polyaniline emeraldine base films. *Synth. Met.* **140**, 49 (2004)
- D. Verma, V. Dutta, Role of novel microstructure of polyaniline-CSA thin film in ammonia sensing at room temperature. *Sens. Actuators B* **134**, 373 (2008)
- L.F. Malmonge, G.A. Lopes, S.C. Langiano, J.A. Malmonge, J.M.M. Cordeiro, L.H.C. Mattoso, A new route to obtain PVDF/PANI conducting blends. *Eur. Polym. J.* **42**, 3108 (2006)
- S.M. Ebrahim, A. Gad, A. Morsy, Highly crystalline and soluble dodecylbenzene sulfonic acid doped poly(o-toluidine). *Synth. Met.* **160**, 2658 (2010)
- P. Liu, Synthesis and characterization of organo-soluble conducting polyaniline doped with oleic acid. *Synth. Met.* **159**, 148 (2009)
- M.V. Kulkarni, A.K. Viswanath, Comparative studies of chemically synthesized polyaniline and (poly(o-toluidine) doped with p-toluene sulphonic acid). *Eur. Polym. J.* **40**, 379 (2004)
- I. Sasaki, J. Janata, M. Josowicz, Stabilization of electronic properties of (IR)-(-)-10-camphorsulfonic acid doped polyaniline by UV irradiation. *Polym. Degrad. Stab.* **92**, 1408 (2007)
- T. Chen, C. Dong, X. Li, J. Gao, Thermal degradation mechanism of dodecylbenzene sulfonic acid-hydrochloric acid co-doped polyaniline. *Polym. Degrad. Stab.* **94**, 1788 (2009)
- C. Basavaraja, R. Pierson, D.S. Huh, A. Venkataraman, S. Basavaraja, Studies on properties of polyaniline-dodecylbenzene sulfonic acid composite films synthesized using different oxidants. *Macromol. Res.* **17**, 609 (2009)
- H. Pei, L. Hong, J.Y. Lee, Effects of polyaniline chain structures on proton conduction in a PEM host matrix. *J. Membr. Sci.* **307**, 126 (2008)
- L. Zhang, L. Zhang, M. Wan, Molybdic acid doped polyaniline micro/nanostructures via a self-assembly process. *Eur. Polym. J.* **44**, 2040 (2008)
- E.N. Konyushenko, J. Stejskal, M. Trchová, N.V. Blinova, P. Holler, Polymerization of aniline in ice. *Synth. Met.* **158**, 927 (2008)
- P. Bober, M. Trchová, J. Prokes, M. Vaga, J. Stejska, Polyaniline-silver composites prepared by the oxidation of aniline with silver nitrate in solutions of sulfonic acids. *Electrochim. Acta* **56**, 3580 (2011)