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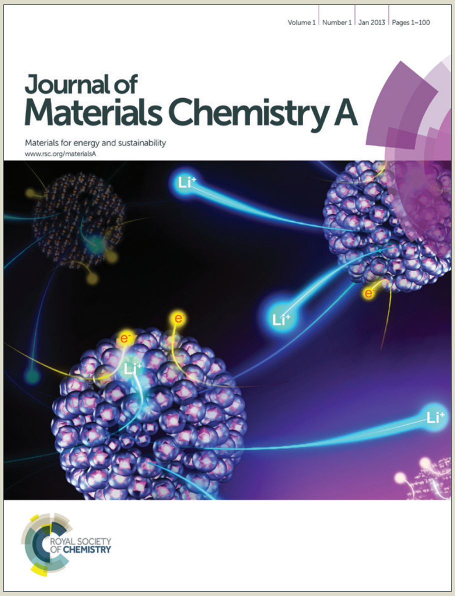

"Hybrid Materials of Polyaniline and Acidic Hexaniobate Nanoscrolls: High polaron formation and improved thermal properties"

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Abstract

The study of hybrid materials of components combined in nanoscale range is an active field due to the possibility of new technologically relevant applications. This paper reports the structural characterization and investigation of the thermal properties of a new hybrid material formed by the mixture of dispersions of polyaniline (PANI), a conducting polymer, and acidic hexaniobate nanoscrolls (NbONsc), a semiconducting metal oxide. Resonance Raman spectra indicate that the relative population polaronic to bipolaronic segments in the hybrid material prepared at pH 2.5 is higher than indicated for pristine PANI prepared in 1.0 mol L^{-1} hydrochloric acid. Although the hybrid material was prepared at pH 2.5, electron paramagnetic resonance spectra indicate similar polaron populations comparing with pristine PANI, which indicate that the hybrid material presents a high conversion of bipolaronic to polaronic segments. Such features were attributed to a strong interaction between the PANI and the acidic NbONsc, inducing conformational changes of the polymeric chains and high formation of polarons at pH 2.5 (secondary doping). Thermogravimetric analyses showed that the on-set temperatures of polymer decomposition in the hybrid materials are *ca.* 15 °C higher comparing with pristine PANI. More interestingly, RR spectroscopy data showed that PANI in the presence of NbONsc remains in its doped form even after heating at 150 °C for 90 min, which was not observed for the pristine polymer. Based on a simple experimental procedure reported here, thermally stable hybrid nanomaterials of highly doped PANI and acidic hexaniobate nanoscrolls were successfully prepared and characterized and exhibit potential applications for electronic devices.

1. Introduction

Polyaniline (PANI) has shown great potential for development of materials for different fields such as chemical sensing,[1-2] energy storage,[3-6] and memory devices.[7-8] The conducting form of PANI, the emeraldine salt (PANI-ES), is obtained by the acid doping of its non-conducting form, the emeraldine base (PANI-EB). The great enhancement of the electrical properties of PANI upon doping process is mainly attributed to the formation of polaronic species (also known as radical-cations),[9-13] as schematized in figure 1 (adapted from refs 9 and 10). The acid doping of PANI is initiated by the protonation of imine nitrogen atoms of PANI-EB, resulting in paired spin species (diamagnetic species), the bipolarons (also known as dications). These structures may be converted to polarons, which are unpaired spin species (paramagnetic species), by an internal redox process.[9-13] Although the electrical properties of PANI are strongly associated to the presence of polarons the bipolaron-polaron relation is important to characterize the doping state of PANI-based materials. Figure 1 also shows that further protonation of the polymeric chains (called overdoping) may lead to the decrease of polaron population, due its conversion to bipolarons. Considering that the conduction mechanism is associated to polarons, the overdoping of polymeric chains is unfavorable for the electronic properties of PANI. This effect was reported for PANI doped in very high acidic media, such as 75% sulfuric acid.[13] Besides of protonation aspects, conformational changes of the polymeric chains may also occur, inducing a high formation of polarons by the organization of the polymer backbone. Therefore, this effect (called secondary doping) may lead to a great improvement of the electrical properties of PANI and is one of the most desirable features for designing hybrid materials of PANI.[14-15]

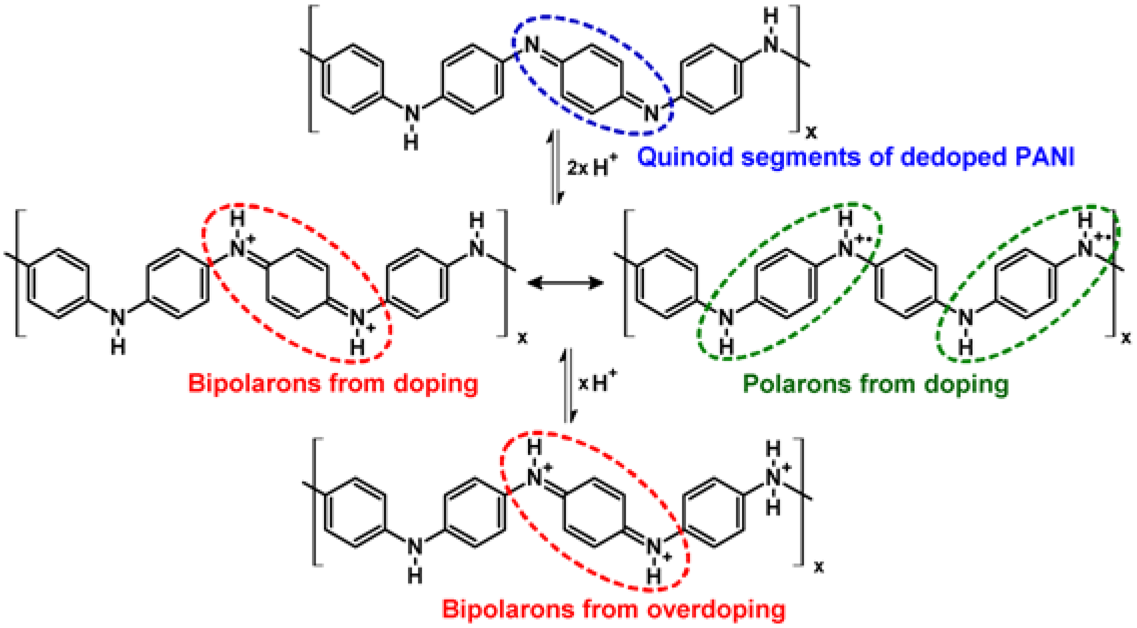

Figure 1. Scheme of the doping and overdoping processes of polyaniline and formation of the bipolaron and polaron segments. The anions are not shown. Adapted from refs 9 and 10.

Considering that PANI-based materials have been used to produce many electronic devices, the thermal stability of doped form of PANI is an important issue for many practical applications. Most of the procedures described in literature reports hydrochloric acid media for preparation and/or doping of PANI chains. Therefore, polyaniline usually suffers dedoping process after thermal treatments at 100-200 °C due to high volatility of dopant (hydrogen chloride).[16-17]

Combination of PANI and inorganic layered materials (ILMs) in nanoscale range may result in hybrid materials which present improved features, such as electrochemical, mechanical or thermal behavior, or novel properties not observed for the isolated components.[18-21] An ease procedure to preparation of hybrid materials is the direct addition of dispersion of PANI to the dispersion of delaminated (or exfoliated) particles of the inorganic layered material. This synthetic route presents some advantages comparing to classical *in-situ* polymerization of intercalated monomers as, for example, better control of PANI/ILM weight ratio by choice of proportion of dispersions and absence of not desired by-products of polymerization process, such as low molar weight oligomers.

Hexaniobate is a semiconducting metal oxide which structure is constituted of negatively charged layers of [NbO_6] octahedral units jointed by corners and edges, and interlayer cations, such as potassium ions, of the precursor form $K_4Nb_6O_{17}$.[22-24] The acidic form of hexaniobate, $H_2K_2Nb_6O_{17}$, can be easily prepared by a cation-exchange reaction.[24-25] Moreover, it has been reported that protonic niobates and titanoniobates are promising materials to produce solid acid catalysts for different chemical reactions due to their high acidic surfaces.[26-27] Therefore, concerning the application of hexaniobate for designing hybrid materials with PANI, $H_2K_2Nb_6O_{17}$ form is very interesting because it could also act as a doping agent for the polymeric chains.

New possibilities of applications of layered materials are achieved by exfoliation (or delamination) processes, producing interesting nanoparticles and giving rise to novel nanodevices.[28] Several authors have reported that the treatment of hexaniobate with *n*-alkylamines and tetra(*n*-alkyl)ammonium hydroxides is a straightforward procedure to obtain stable colloidal dispersions of the exfoliate nanoparticles.[28-31] It has been reported that treatment of $K_4Nb_6O_{17}$ with tetra(*n*-butyl)ammonium hydroxide (TBAOH) results in the exfoliation and curling of the delaminated layers, producing 1D nanoparticles, called hexaniobate nanoscrolls (NbONsc). Our group has shown that the treatment of $H_2K_2Nb_6O_{17}$ with TBAOH is also an efficient procedure to provide colloidal dispersions of the protonic hexaniobate nanoscrolls (schematized in figure 2).[32]

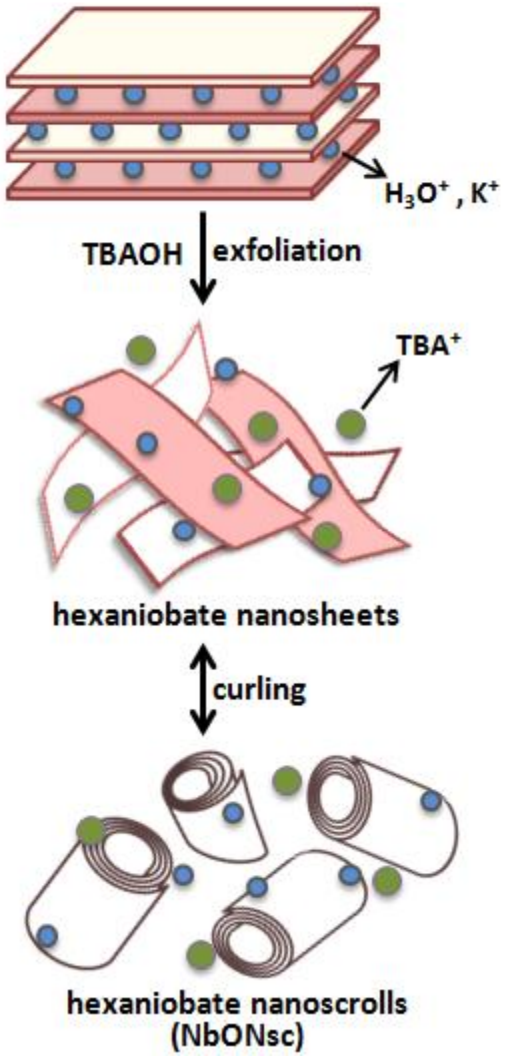

Figure 2. Scheme of exfoliation process of lamellar hexaniobate and formation of hexaniobate nanosheets and nanoscrolls (NbONsc).

According to our previous paper,[32] hybrid films of PANI and NbONsc prepared by layer-by-layer assembly technique presented interesting electrochromic features, which were attributed to the high polaron formation induced by a strong interaction between the components of the material. This paper reports a simple preparation and spectroscopic characterization of a novel hybrid nanomaterial of polyaniline and scrolled nanostructures of protonic hexaniobate, $H_2K_2Nb_6O_{17}$. The thermal properties of this hybrid material were also investigated.

2. Experimental Section

Aniline (Merck) was distilled under reduced pressure prior to use. Niobium pentoxide (CBMM - Companhia Brasileira de Metalurgia e Mineração) was used as received. TBAOH aqueous solution (Sigma-Aldrich, 55%) was used as received. All other chemicals (Merck) were also used as received.

2.1. Synthesis of polyanilines and dispersion of emeraldine salt polyaniline (PANI-ES)

PANI-ES was synthesized following well-known chemical route of oxidative polymerization of aniline with ammonium peroxydisulfate in 1 mol L^{-1} hydrochloric acid (pH *ca.* 0).[33-35] PANI-EB was prepared by dedoping PANI-ES in 0.1 mol L^{-1} NH_3 solution. PANI-ES dispersion (pH 2.5) in water/*N*,*N*-dimethylacetamide (9/1 in volume) was prepared following procedure described in literature.[19, 36] The concentration of the dispersions used for preparation of the hybrid materials was 4.2×10^{-3} mol L^{-1}, considering the tetrameric constitutional repeating unit of PANI (see figure 1). A detailed description of the experimental procedures is presented in Supporting Information.

2.2 Syntheses of hexaniobates and colloidal dispersion of hexaniobate nanoscrolls

Precursor form of hexaniobate ($K_4Nb_6O_{17}$) was synthesized by usual ceramic method, heating stoichiometric mixture of Nb_2O_5 and K_2CO_3 at 1100 °C for two steps of 5 hours each.[24, 37] The obtaining of hydrous phase $K_4Nb_6O_{17}\cdot 3H_2O$ was confirmed by X-ray diffractometry (XRD) data (d_{040} peak at 9.3 Å). The protonic hexaniobate ($H_2K_2Nb_6O_{17}$) was prepared by treating $K_4Nb_6O_{17}$ with 6 mol L^{-1} HNO_3 solution (reflux at 60 °C for 6 days).[24, 31, 37] The hydrous phase $H_2K_2Nb_6O_{17}\cdot H_2O$ was confirmed by XRD (d_{040} peak at 7.9 Å) and thermogravimetric analysis (TGA) data. Colloidal dispersion of hexaniobate nanoscrolls (NbONsc) was prepared according to Shiguihara *et al.*,[31, 38] by treating $H_2K_2Nb_6O_{17}$ with TBAOH solution, using TBA^+/H^+-hexaniobate molar ratio of 0.75. The concentration of NbONsc in the dispersion was *ca.* 1.2 g L^{-1}. For the preparation of the hybrid materials the pH of the dispersion was adjusted to 2.5. A detailed description of the experimental procedures is presented in Supporting Information.

2.3 Preparation of the hybrid materials of doped polyaniline and hexaniobate nanoscrolls

The hybrid materials were prepared by the simple mixture of the dispersions at pH 2.5, as schematized in figure 3. Approximately, 17.0 mL of PANI dispersion was slowly added to 55.0 mL of NbONsc, and stirred for 48 h. Afterwards, the mixture volume was divided in two equal portions. The first portion was centrifuged (7500 rpm for 30 min), and the obtained solid was named PNb(pH2.5). For the second portion, the pH of the mixture was reduced to 0.1 (similar acidity of preparation media of pristine PANI) by addition of drops of hydrochloric acid solution, and then centrifuged. The solid obtained by this route was named PNb(pH0.1). Therefore, the hybrid materials of doped PANI and hexaniobate nanoscrolls were prepared at two acidity conditions (2.5 and 0.1) in order to study the protonation/doping behavior of the polymer in the presence of the metal oxide nanoparticles and to compare their structural features with pristine PANI (prepared in HCl 1 mol L^{-1}, pH *ca.* 0).

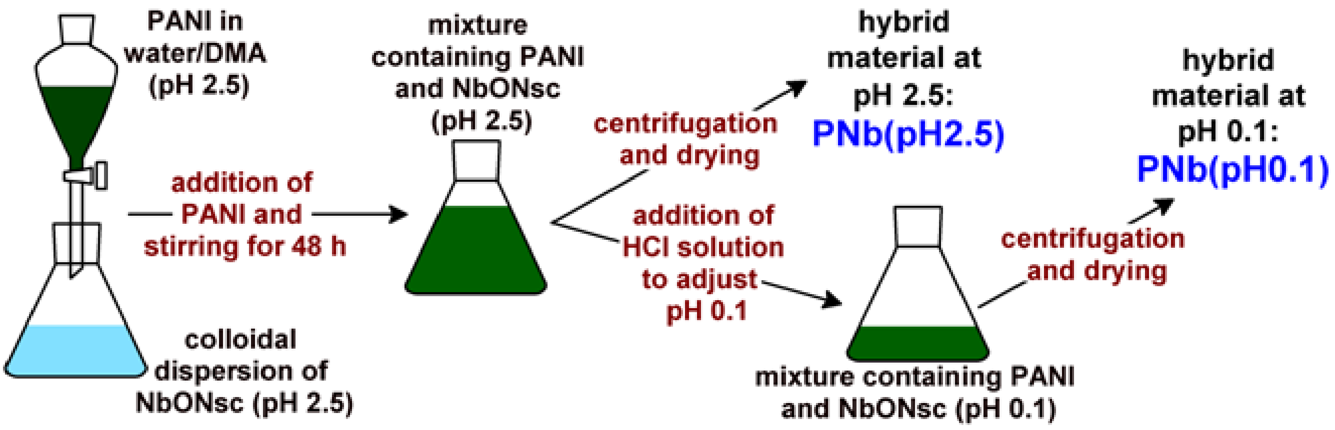

Figure 3. Scheme of preparation procedure of the hybrid materials PNb(pH2.5) and PN(pH0.1). NbONsc = hexaniobate nanoscrolls. DMA = *N*,*N*-dimethylacetamide.

2.4. Characterization

Morphological characterization was performed for the samples (pristine polyaniline and hybrid materials) dispersed in acetone and deposited on silicon substrates, which were attached to aluminum stubs by a double-sided copper tape. For hexaniobate sample, the colloidal dispersion of NbONsc (pH adjusted to 2.5) was directly deposited on silicon substrates. Scanning Electron Microscopy images (SEM images) were recorded in a Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-7410) from Central Analítica do Instituto de Química – Universidade de São Paulo (CA-IQUSP), using acceleration voltages of 3-5 kV. Energy dispersive X-ray (EDX) spectra were also acquired for different points at the same regions of the SEI images to probe the presence of niobium atoms in the materials. For this purpose, acceleration voltages of 7-8 kV were used.

Resonance Raman (RR) spectra were obtained at 632.8 nm excitation radiation (He-Ne laser, Renishaw 7N1753) in a Renishaw Raman imaging microscope (inVia) equipped with a Leica microscope and a CCD detector. The spectra were recorded using a 50x lens (Olympus SM Plan, N.A. 0.55) and laser power was kept below 50 μW to avoid sample photodegradation. Peak fitting of Gaussian bands was performed by using GRAMS/AI software (version 9.1).

Electron paramagnetic resonance (EPR) spectra were recorded for solid samples at 77 K (liquid nitrogen) on a Bruker EMX spectrometer operating at X-band frequency, and using α,α'-diphenyl-β-picrylhydrazyl (DPPH) as frequency calibrant (*g* factor of 2,0036). For the proper analysis of the EPR data, the measurements were performed by analyzing samples of known weights and the results were discussed in term of the values of the integral areas of the EPR signals normalized by the weight of polymer in each sample (DI/m values). The weight of polymer contained in each sample was determined from thermogravimetric analysis data. For details of sample weights and polymer content in each sample, see Supporting Information (table S1). The normalization procedure is required considering that the samples present different polymer contents. Integral areas of the EPR signals were determined by using Bruker software (double integration procedure).

2.5. Thermal analyses and heating treatments

The mass spectrometry-coupled thermogravimetric analyses (TGA-MS) were performed by heating *ca.* 5 mg of the samples from room temperature to 1000 °C. The TGA-MS curves were recorded on a Netzsch thermoanalyser model TGA/DSC 490 PC Luxx coupled to an Aëolos 403 C mass spectrometer, under synthetic air flow of 50 mL min^{-1} and heating rate of 10 °C min^{-1}. The on-set temperatures of irreversible decomposition of the polymeric chains (T_d) were determined by using Netzsch Proteus Thermal Analysis software. The heating treatments *ca.* 5 mg of the samples were also performed on the Netzsch thermoanalyser by isothermal heating at 150 °C during 90 min, under synthetic air flow of 50 mL min^{-1} and heating rate of 10 °C min^{-1}.

Afterwards, the heated samples were collected for structural characterization by Raman spectroscopy.

3. Results and Discussion

The morphology of the hybrid materials was characterized by scanning electron microscopy (SEM). Figure 4(a) presents SEM image of pristine polyaniline (PANI-ES), showing that PANI-ES consists of granular and irregular particles, which is in agreement with other reported papers.[39-40] SEM image of NbONsc sample in figure 4(b) is also in accordance with literature,[29, 41-45] and shows that exfoliation of $H_2K_2Nb_6O_{17}$ results in nanoparticles called hexaniobate nanoscrolls (NbONsc), which present high aspect ratio (length/diameter ratio). According to our previous paper, such nanoscrolls present broad diameter distribution and mean diameter of *ca.* 26 nm.[32] Figure 4(c) shows the SEM image of the hybrid material PNb(pH2.5), which presents regions containing particles of high aspect ratio dispersed in irregular material. Such particles exhibit diameters ranging from 20 to 35 nm and are consistent with the NbONsc. Similar results were obtained for PNb(pH0.1) hybrid materials, as presented in Supporting Information (figures S1).

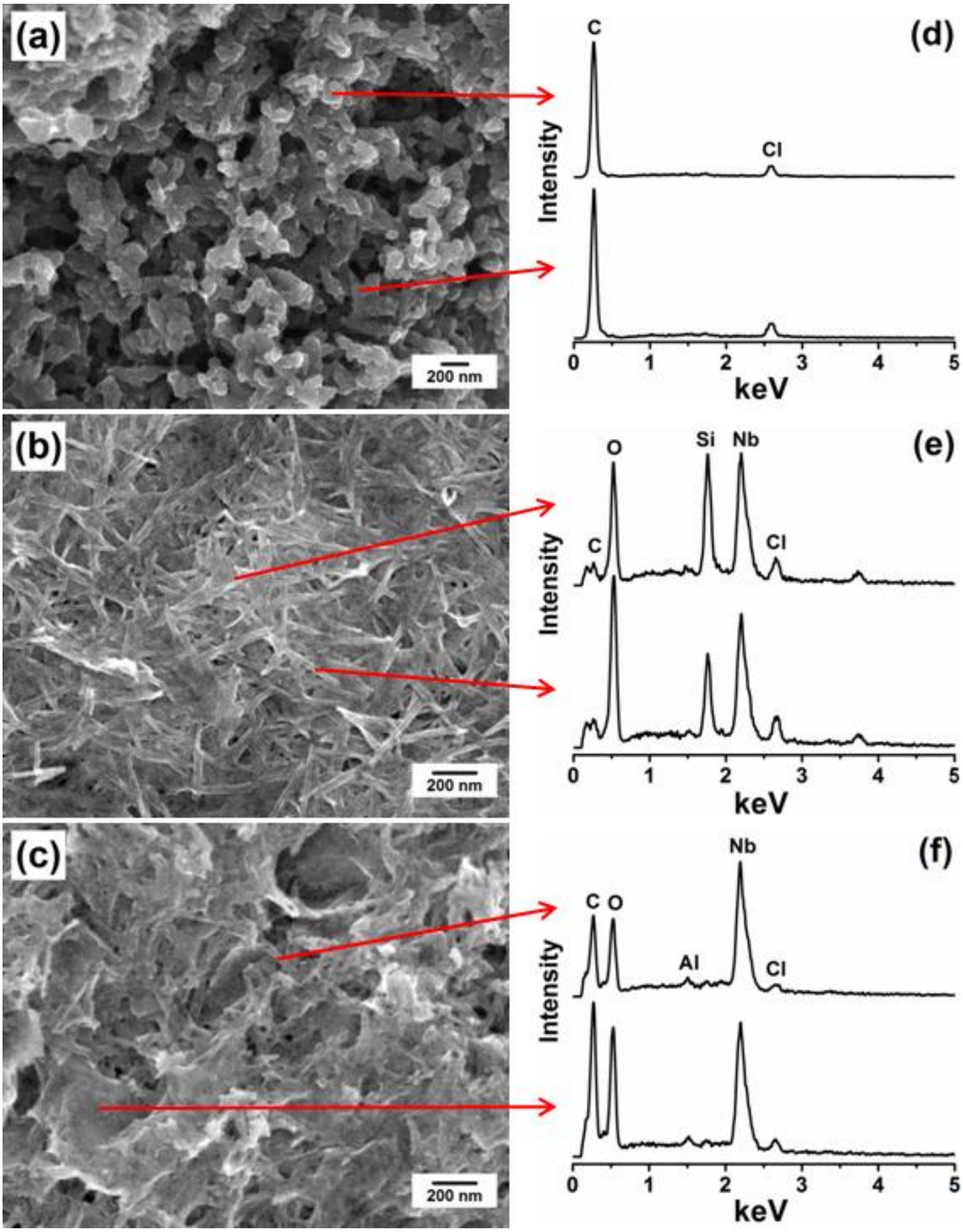

Figure 4. SEM images and EDX spectra of (a, d) PANI-ES, (b, e) NbONsc and (c, f) PNb(pH2.5). SEM image and EDX spectra of hybrid material PNb(pH0.1) are shown in Supporting Information (Figure S1).

In order to confirm the compositional homogeneity of the hybrid materials in the micro/nanoscale range, energy dispersive X-ray (EDX) spectra were acquired for two different regions each sample, as presented in figure 4(d-f). As expected, EDX spectra of PANI-ES (figure 4(d)) only present peaks at 0.3 and 2.7 keV, assigned to carbon (K_α emission) and chlorine (K_α emission) atoms,[46] respectively. The high intensities for the low-energy peaks (lesser than 1 keV) are not reliable for quantitative analysis of the elemental composition due to instrumental factors, such as interference of the emitted photons and sample-instrument interaction.[46] In addition to carbon and oxygen peaks at 0.3 and 0.5 keV, respectively, EDX spectra of NbONsc (figure 4(e)) present high intensity peaks at 1.8 and 2.2 keV, assigned to silicon (K_α emission) and niobium (L_α emission) atoms,[46] respectively, and also low intensity peaks at 2.7 and 3.7 keV assigned to chlorine and potassium atoms,[46] respectively. The observation of niobium and potassium peaks is consistent with the hexaniobate form ($H_2K_2Nb_6O_{17}$), while chlorine and carbon peaks could be attributed to tetra(*n*-butyl)ammonium and chloride ions from NbONsc dispersion, which pH was adjusted to 2.5 by addition of hydrochloric acid. The presence of silicon peak is attributed to the Si substrate, which was only observed for NbONsc sample due to its low thickness after deposition on substrate. Finally, EDX spectra of PNb(pH2.5) show peaks at 0.3, 0.5, 2.2 and 2.7 keV, assigned to carbon, oxygen, niobium and chlorine atoms, in addition to a peak at 1.5 keV, which could be assigned to aluminum,[46] probably from the sample holder (stubs). EDX spectra were also recorded for PNb(pH0.1) sample and were very similar to those obtained for the hybrid material prepared at pH 2.5 (Supporting Information, figure S1).

Therefore, EDX spectroscopy data and SEM images of the hybrid materials indicate that hexaniobate nanoparticles are homogeneously dispersed into a matrix of irregular morphology, attributed to PANI. As mentioned previously, such combination of NbONsc and PANI in nanoscale range has been observed for hybrid films prepared by layer-by-layer assembly technique.[32]

Figure 5(a) shows the resonance Raman (RR) spectra of PANI-ES, PNb(pH2.5) and PNb(pH0.1) in 1700-1000 cm^{-1} range. All spectral features observed at 1700-1000 cm^{-1} range for the hybrid materials are exclusively due to polyaniline because hexaniobate presents strong Raman bands only below 1000 cm^{-1},[47-48] and also this inorganic material is not in resonance condition at 632.8 nm excitation radiation. Resonance Raman spectrum of PNb(pH2.5) presents the characteristic bands of doped polyaniline at 1618-1590, 1506-1485, 1335, 1257 and 1170 cm^{-1}, which can be associated to bands in the spectrum of PANI-ES at 1619-1579 (νC-C), 1515-1483 (βN-H and νC-C), 1336-1317 (νC-$N^{\bullet+}$), 1253 (νC-N) and 1164 cm^{-1} (βC-H).[49-52] In order to study the protonation/doping behavior of PANI in the presence of the NbONsc, hybrid materials were also prepared at pH 0.1, similar acidity of preparation media of pristine PANI (pH *ca.* 0), as described in experimental part (hybrid material PNb(pH0.1)). The RR spectrum of PNb(pH0.1), presents a very similar feature comparing with the hybrid material prepared at pH 2.5. However, minor differences observed, such as the broadening of the bands at 1630-1570 and 1520-1480 cm^{-1} could indicate changes of PANI structure in the hybrid materials prepared at different pHs.

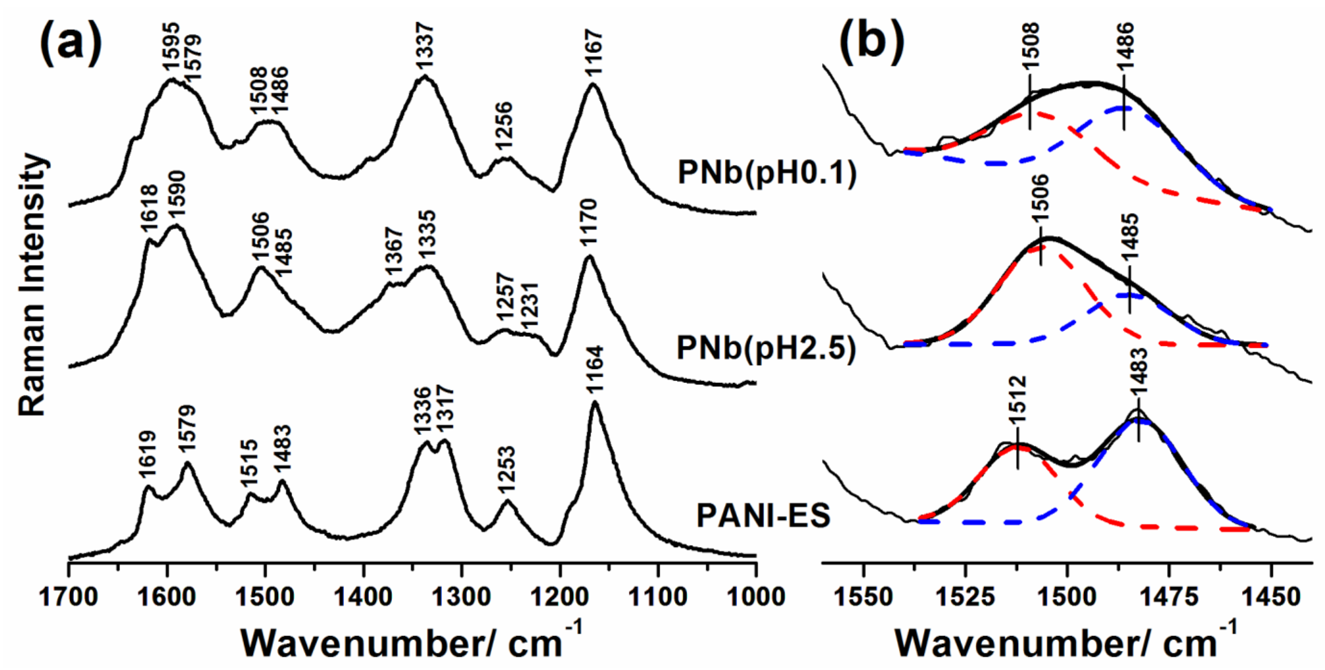

Figure 5. (a) Resonance Raman spectra (λ_0 = 632.8 nm) of PANI-ES and the hybrid materials PNb(pH2.5) and PNb(pH0.1) at 1700-1000 cm^{-1} range. (b) Peak fitting of Raman bands at 1550-1450 cm^{-1} range (dashed lines).

Figure 5(b) shows in detail the 1550-1450 cm^{-1} range of RR spectra of PANI-ES, PNb(pH2.5) and PNb(pH0.1). At this spectral range, the fitted Gaussian bands can be assigned to polaronic or bipolaronic segments,[49-52] thus providing important information on the relative population of the charge carriers in the polymeric chains. The fitted band at higher wavenumber (1512 cm^{-1} for PANI-ES) is assigned to the βN-H vibration modes of the polarons, while the band at lower wavenumber (1483 cm^{-1} for PANI-ES) is due to νC-C of the bipolarons.[49-50] According to figure 5(b), RR spectrum of PNb(pH2.5) shows higher intensity ratio of bands (1506 cm^{-1}/1485 cm^{-1}) than that observed for PANI-ES (1512 cm^{-1}/1483 cm^{-1}). These results show that PNb(pH2.5) presents a higher relative population of polaronic segments comparing with PANI-ES, suggesting a high conversion of bipolarons to polarons in the hybrid material.

Considering that PANI-ES is prepared in a much stronger acidic medium (HCl 1 mol L^{-1}) than PNb(pH2.5), such unexpected increase of the relative population of polaronic segments in the hybrid material could be attributed to a strong interaction between PANI and the NbONsc. This interaction induces conformational changes in the polymeric chains, increasing the population of polaron segments (secondary doping). The high bipolaron-polaron conversion has been reported by our group for hybrid layer-by-layer films of PANI and NbONsc.[32] For PNb(pH0.1) hybrid material, figure 5(b) shows that the intensity ratio of bands (1508 cm^{-1}/1486 cm^{-1}) is lower than the observed for PNb(pH2.5), indicating a decrease of the relative population of the polaronic segments when the hybrid material is prepared in strong acidic medium (pH 0.1).

Although RR spectroscopy identifies the polymeric segments and gives their relative populations, for a direct measurement of the polaronic population in the materials the Electron Paramagnetic Resonance (EPR) spectroscopy must be used. Figure 6 shows the EPR spectra of hexaniobate, PANI-ES, PNb(pH2.5) and PNb(pH0.1). As expected, hexaniobate does not present EPR signal, due to absence of unpaired spins (Nb(V) has a $4d^0$ configuration). For PANI-ES and hybrid materials, EPR spectra exhibit very narrow signals at $g = 2,002$. Such EPR signals are typical of organic radicals,[12, 53-56] and can be assigned to the polaronic segments of PANI. According to EPR spectra, DI/m values (integral areas of the EPR signals normalized by the weight of polymer) for PANI-ES and PNb(pH2.5) are very similar, 54 and 55 mg^{-1}, respectively, which indicate that the polaronic populations of PANI-ES and PNb(pH2.5) are also similar. Such feature was not expected, since the hybrid material was prepared in a very lower acidity medium (pH2.5) than PANI-ES (pH *ca.* 0). The comparison of DI/m values for PNb(pH2.5) and PNb(pH0.1), 55 and 29 mg^{-1}, respectively, indicates a significant decrease of the polaron populations when the hybrid materials is prepared in a strong acidic medium (pH 0.1). Such results indicate a higher conversion of polarons to bipolarons in the PNb(pH0.1) hybrid material. Moreover, the comparison of DI/m values for PANI-ES and PNb(pH0.1) clearly indicates that, although these materials were prepared at the same acidity medium, the hybrid material present a lower polaron population. Therefore, EPR data are in accordance with RR spectra and suggest a strong interaction between polyaniline chains and hexaniobate nanoscrolls, which induces a high formation of the polaronic segments in a lower acidity medium (pH 2.5), but a decrease of the polaronic population in a higher acidity medium (pH 0.1). The latter feature can be attributed by the association of the high acidity of the preparation medium and high surface acidity of the NbONsc, which may lead to an overdoping of the of the PANI chains in the PNb(pH0.1), as schematized in figure 1. Furthermore, the EPR data in figure 6 clearly show that the values of EPR linewidth (ΔH_{pp}) for the hybrid materials are lower than for PANI-ES (3.6, 4.7 and 9.3 G, for PNb(pH2.5), PNb(pH0.1) and PANI-ES, respectively). These results indicate that NbONsc also induce an increase of the electronic delocalization of the polarons.[54, 57] Therefore, RR and EPR techniques indicate a strong interaction between the components of the hybrid materials, suggesting a secondary doping of polyaniline chains in the presence of the hexaniobate nanostructures.

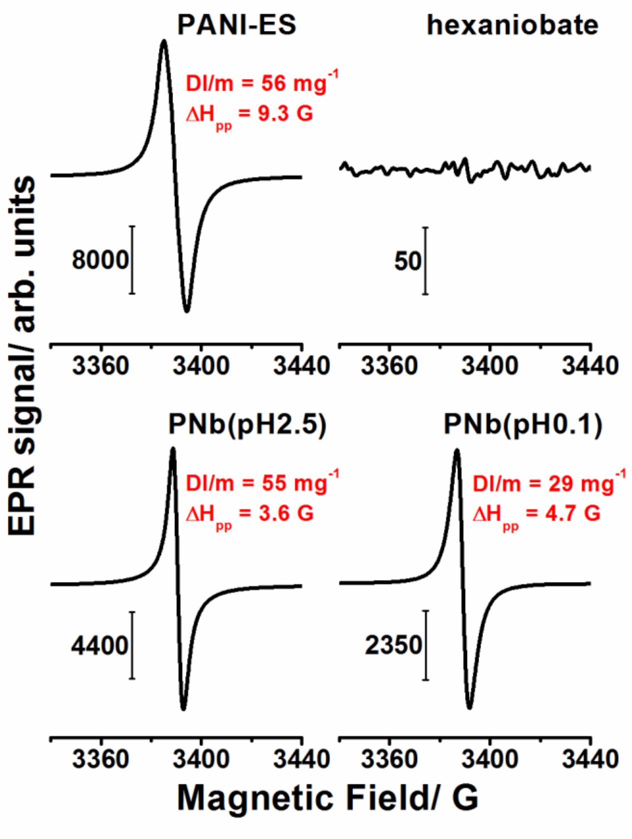

Figure 6. EPR spectra of PANI-ES, hexaniobate and hybrid materials PNb(pH2.5) and PNb(pH0.1). DI/m and ΔH_{pp} are the values of the EPR signal (integral areas of the EPR signals normalized by the weight of polymer) and the EPR linewidth, respectively. For details of sample weights and polymer contents, see Supporting Information (table S1).

The thermal properties of the polyaniline/hexaniobate hybrid materials were also investigated. Figure 7(a) presents the thermogravimetric analysis (TGA) curves of PANI-ES, hexaniobate, PNb(pH2.5) and PNb(pH0.1). According to TGA curves, hexaniobate presents a very high thermal stability comparing with PANI-ES and hybrid materials. Hexaniobate undergoes mass losses of only 5 and 2% at the temperature ranges of 25-300 and 300-800 °C, respectively, which are attributed to water loss from dehydration and dehydroxylation processes, respectively.[24]

It is well know that HCl-doped PANI presents a complex TGA curve, showing mainly three superimposed thermal processes of mass loss (25-120, 120-300 and 300-700 °C). The first event is assigned to the moiety loss and evolution of unbound and adsorbed hydrogen chloride, while the second step is due to the loss of HCl dopant strongly bound to polymeric chains (a process known as thermal dedoping).[16-17, 58-60] The last and most prominent mass loss event (*ca.* 84%) is attributed to the complex and irreversible process of decomposition of the polymeric chains.[17, 58-60] It is important to mention that other thermal events also occur during heating of polyaniline, but they do not lead to significant mass loss, such as chain scission and cross-linking formation.[61-62]

Analogously to PANI-ES, TGA curves of the hybrid materials PNb(pH2.5) and PNb(pH0.1) present mass loss events due to moiety loss, thermal dedoping and polymer decomposition, but at slightly different temperatures ranges (25-120, 120-250 and 250-600 °C, respectively). Moreover, TGA data show that hybrid materials present residual masses at 800 °C, which can be attributed to the hexaniobate contents in the hybrid materials. According to figure 7(a), the polymer/hexaniobate contents in PNb(pH2.5) and PNb(pH0.1) are 35%/55% and 32%/57%, respectively. For details of the TGA curves and determination of the polymer/hexaniobate contents, see Supporting Information (figure S2).

Figure 7(b) shows the MS curves of hexaniobate, PANI-ES and hybrid materials recorded during TGA measurements for ions of *m/z* equal to 44, which can be attributed to the formation of CO_2 during the heating of the samples. MS curves of PANI-ES and hybrid materials indicate the formation of ions of *m/z* equal 44 above 250 °C, in contrast to hexaniobate, which does not exhibit ion formation at the investigated temperature range. These results show that the formation of CO_2 occurs for PANI-ES and hybrid materials during the main weight loss step (*ca.* 250-700 °C), as presented in figure 7(a).

Therefore, MS curves indicated that the main thermal event of weight loss is due to the irreversible decomposition of polymeric chains in PANI-ES and hybrid materials.

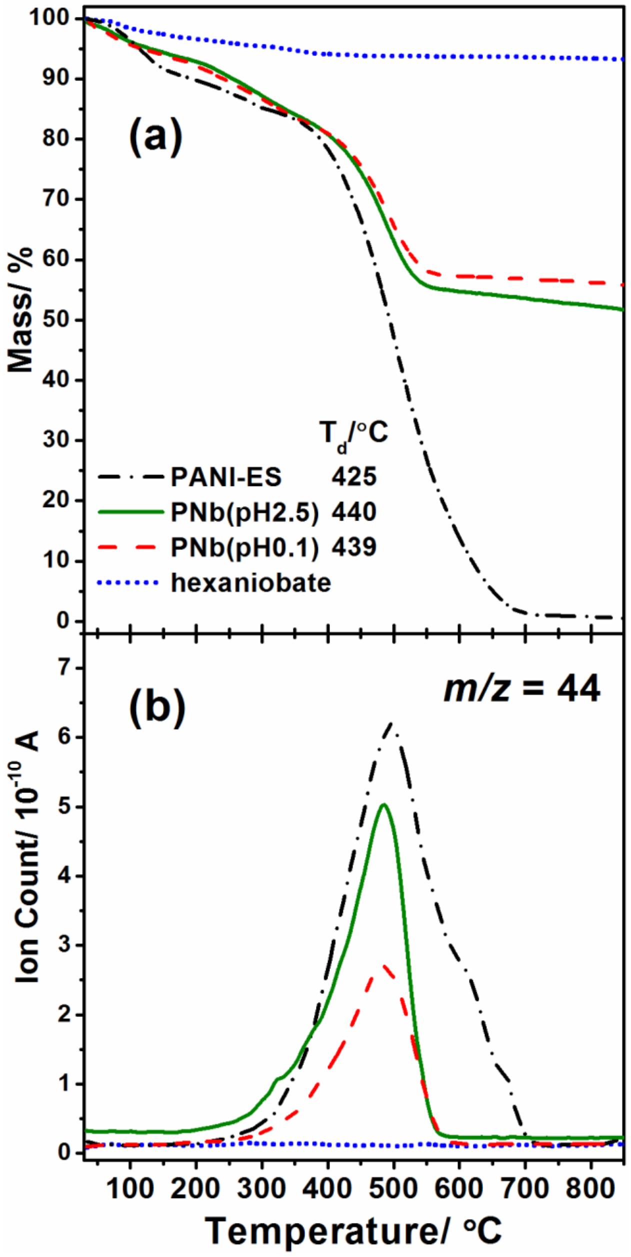

Figure 7. (a) TGA curves and (b) MS curves (*m/z* = 44) of PANI-ES, hybrid materials PNb(pH2.5) and PNb(pH0.1), and hexaniobate. T_d are the on-set temperatures of irreversible decomposition of the PANI chains. Detailed information of TGA data are available in Supporting Information (figure S2).

Figure 7(a) also shows that the on-set temperatures of polymer decomposition (T_d) in PANI-ES, PNb(pH2.5) and PNb(pH0.1) are 425, 440 and 439 °C, respectively. Considering that TGA curves were recorded for very similar weights of samples and, consequently, lower polymer weights for the hybrid materials, the enhancement of *ca.* 15 °C on the T_d for PNb(pH2.5) and PNb(pH0.1) are significant. Therefore, these results reveal that thermal stability of the PANI chains are improved in the presence of the hexaniobate.

Considering that several electrical devices may require operation at higher temperatures than room-temperature, it is convenient that PANI-based materials remains in its doped form upon heating. For this purpose, PANI-ES and hybrid materials were submitted to heating treatments (150 °C during 90 min) and characterized by RR spectroscopy, as shown in figure 8. RR spectrum of heated PANI-ES shows the decreasing of the relative intensity of the band of doped PANI at 1333 cm^{-1} and the rising of the bands at 1470 and 1221 cm^{-1}, which are observed in the RR spectrum of the undoped polyaniline (PANI-EB) and assigned to $\nu C{=}N$ and $\nu C{-}N$, respectively.[63] Thus, these results show that pristine polyaniline undergoes thermal dedoping upon the heating treatment. In addition to bands of dedoped PANI, RR spectrum of heated PANI presents bands at 1646, 1399 and 575 cm^{-1}, assigned to phenazine-like structures as thermally induced cross-linking segments.[64-66] However, RR spectrum of PNb(pH2.5) after heating (figure 8) shows that the relative intensity of the band of doped PANI at 1336 cm^{-1} is not significantly affected, and the band (shoulder) due to dedoped PANI at 1471 cm^{-1} presents a low relative intensity. These results clearly demonstrate that polyaniline chains remains in the doped form upon heating treatment in the hybrid material, while pristine PANI is dedoped after the same treatment. Also, PNb(pH2.5) presents cross-linking segments after heating (bands at

1643,1393 and 576 cm^{-1}). A very similar thermal stability was observed for hybrid material prepared at pH 0.1, PNb(pH0.1), revealing that of the doped form of PANI is not appreciably affected by the acidity of the preparation medium (Supporting Information, figure S3). Therefore, TGA and RR results show that hexaniobate nanoscrolls play an important role to the thermal stability of the hybrid materials.

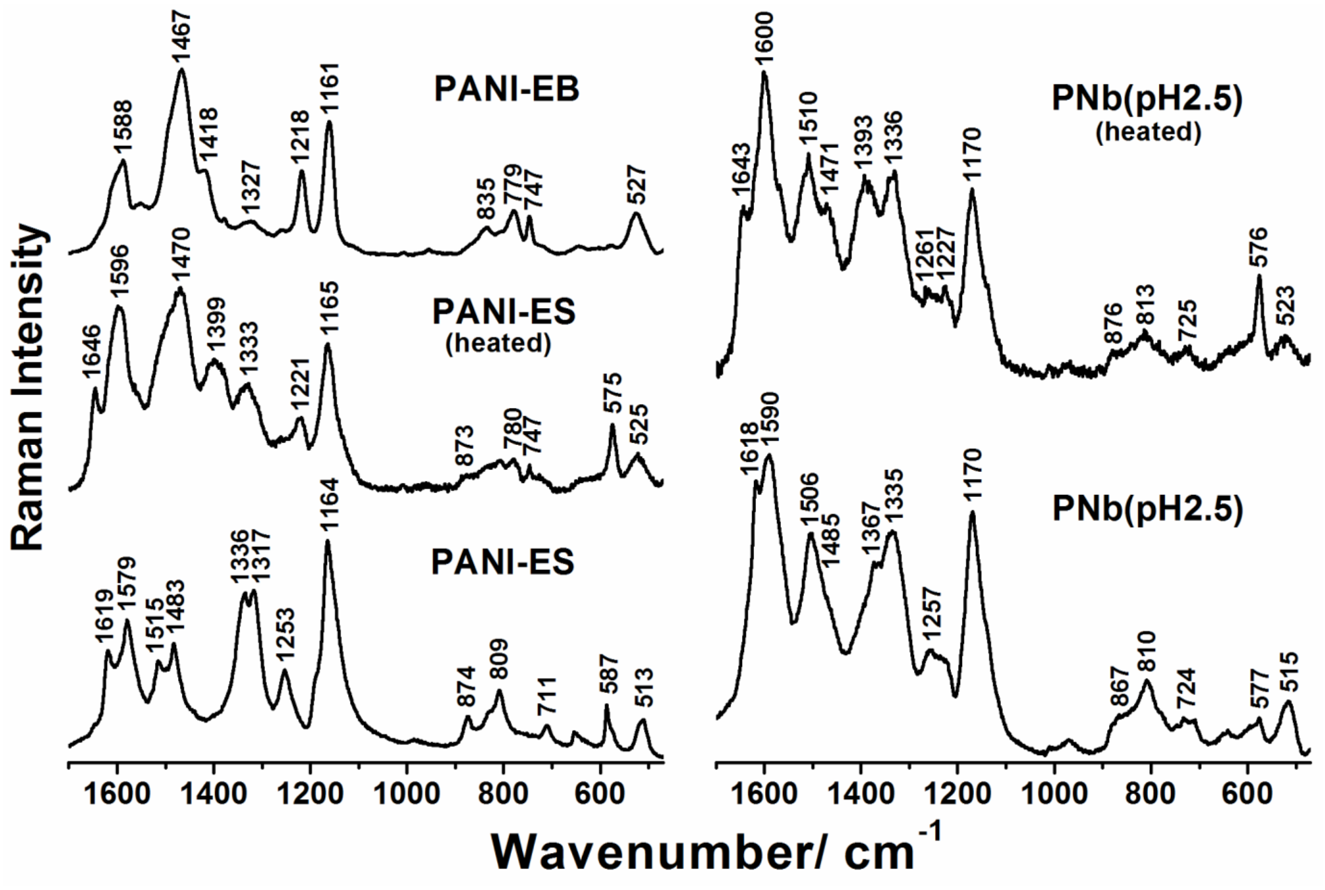

Figure 8. Resonance Raman spectra (λ_0 = 632.8 nm) of PANI-ES and hybrid material PNb(pH2.5) before and after heating treatments (150 °C during 90 min). For comparison purposes, the Raman spectrum of PANI-EB is also presented. See the RR spectrum of hybrid material PNb(pH0.1) in Supporting Information (figure S3).

Conclusions

According to results presented, thermally stable hybrid nanomaterials of highly doped PANI and acidic hexaniobate nanoscrolls were prepared by the mixture of the dispersions of the components. Morphological characterization by scanning electron microscopy and energy dispersive X-ray spectroscopy probed the presence of hexaniobate nanoscrolls in the hybrid materials and showed the combination of the components in the nanoscale range. Resonance Raman spectra indicated that the hybrid material prepared at pH 2.5 presents a high conversion of bipolaronic to polaronic segments comparing with pristine polyaniline (prepared in HCl 1 mol L^{-1}), while the hybrid material prepared at pH 0.1 clearly showed the decrease of the relative population of polarons. Electron paramagnetic resonance data revealed that hybrid material prepared at pH 2.5 presents similar polaron population to pristine polyaniline, whereas the material prepared at pH 0.1 presents lower polaron population. Therefore, spectroscopic data suggest a strong interaction between polyaniline chains and acidic hexaniobate nanoscrolls, which results in a high doping effect to the polymer, leading to the overdoping process of polyaniline at pH 0.1. Thermal properties were investigated and thermogravimetric analysis curves showed that the on-set temperatures of irreversible polymer decomposition in the hybrid materials are *ca.* 15 °C higher comparing with pristine polyaniline. According to RR spectroscopy data, polyaniline in the presence of NbONsc remains in its doped form after heating at 150 °C for 90 min, which was not observed for the pristine polymer. The results reported here indicate the potential applications of these hybrid materials for development of electronic devices.

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References

1. J. Janata and M. Josowicz, *Nat. Mater.*, 2003, **2**, 19-24.
2. S. Virji, J. X. Huang, R. B. Kaner and B. H. Weiller, *Nano Lett.*, 2004, **4**, 491-496.
3. C. Barbero, M. C. Miras, B. Schnyder, O. Haas and R. Kotz, *J. Mater. Chem.*, 1994, **4**, 1775-1783.
4. E. A. Ponzio, T. M. Benedetti and R. M. Torresi, *Electrochim. Acta*, 2007, **52**, 4419-4427.
5. H. Varela, F. Huguenin, M. Malta and R. M. Torresi, *Quim. Nova*, 2002, **25**, 287-299.
6. K. Zhang, L. L. Zhang, X. S. Zhao and J. S. Wu, *Chem. Mater.*, 2010, **22**, 1392-1401.
7. R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner and Yang, *Nano Lett.*, 2005, **5**, 1077-1080.
8. Y. Yang, J. Ouyang, L. Ma, R. J. H. Tseng and C. W. Chu, *Adv. Funct. Mater.*, 2006, **16**, 1001-1014.
9. A. J. Heeger, *Angew. Chem. Int. Ed.*, 2001, **40**, 2591-2611.
10. S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid, *Phys. Rev. Lett.*, 1987, **59**, 1464-1467.
11. A. J. Epstein, J. M. Ginder, F. Zuo, H. S. Woo, D. B. Tanner, A. F. Richter, M. Angelopoulos, W. S. Huang and A. G. MacDiarmid, *Synth. Met.*, 1987, **21**, 63-70.

12. E. M. Genies and M. Lapkowski, *J. Electroanal. Chem.*, 1987, **236**, 199-208.

13. W. S. Huang and A. G. MacDiarmid, *Polymer*, 1993, **34**, 1833-1845.

14. A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1994, **65**, 103-116.

15. A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1995, **69**, 85-92.

16. M. K. Traore, W. T. K. Stevenson, B. J. McCormick, R. C. Dorey, S. Wen and D. Meyers, *Synth. Met.*, 1991, **40**, 137-153.

17. K. Amano, H. Ishikawa, A. Kobayashi, M. Satoh and E. Hasegawa, *Synth. Met.*, 1994, **62**, 229-232.

18. P. Gomez-Romero, *Adv. Mater.*, 2001, **13**, 163-174.

19. C. M. S. Izumi, V. R. L. Constantino and M. L. A. Temperini, *J. Nanosci. Nanotechnol.*, 2007, **8**, 1782-1789.

20. D. Lee and K. Char, *Polym. Degrad. Stab.*, 2002, **75**, 555-560.

21. M. Malta, G. Louarn, N. Errien and R. M. Torresi, *J. Power Sources*, 2006, **156**, 533-540.

22. M. Gasperin and M. T. Lebihan, *J. Solid State Chem.*, 1982, **43**, 346-353.

23. T. Nakato, K. Kuroda and C. Kato, *Chem. Mater.*, 1992, **4**, 128-132.

24. M. A. Bizeto and V. R. L. Constantino, *Mater. Res. Bull.*, 2004, **39**, 1729-1736.

25. M. A. Bizeto, F. P. Christino, M. F. M. Tavares and V. R. L. Constantino, *Quim. Nova*, 2006, **29**, 1215-1220.

26. A. Takagaki, M. Sugisawa, D. Lu, J. N. Kondo, M. Hara, K. Domen and S. Hayashi, *J. Am. Chem. Soc.*, 2003, **125**, 5479-5485.

27. A. S. Dias, S. Lima, D. Carriazo, V. Rives, M. Pillinger and A. A. Valente, *J. Catal.*, 2006, **244**, 230-237.

28. M. A. Bizeto, A. L. Shiguihara and V. R. L. Constantino, *J. Mater. Chem.*, 2009, **19**, 2512-2525.

29. M. A. Bizeto and V. R. L. Constantino, *Mater. Res. Bull.*, 2004, **39**, 1811-1820.

30. K. Domen, Y. Ebina, S. Ikeda, A. Tanaka, J. N. Konda and K. Maruya, *Catal. Today*, 1996, **28**, 167-174.

31. A. L. Shiguihara, M. A. Bizeto and V. R. L. Constantino, *Colloid Surf. A-Physicochem. Eng. Asp.*, 2007, **295**, 123-129.

32. C. H. B. Silva, N. A. Galiote, F. Huguenin, E. Teixeira-Neto, V. R. L. Constantino and M. L. A. Temperini, *J. Mater. Chem.*, 2012, **22**, 14052-14060.

33. A. G. MacDiarmid, J. C. Chiang and A. F. Richter, *Conducting Polymers*, Riedel Publications, Dordrecht, 1987.

34. W. S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. I*, 1986, **82**, 2385-2400.

35. J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, 1986, **13**, 193-205.

36. J. H. Cheung, W. B. Stockton and M. F. Rubner, *Macromolecules*, 1997, **30**, 2712-2716.

37. M. A. Bizeto, D. L. A. de Faria and V. R. L. Constantino, *J. Mater. Sci.*, 2002, **37**, 265-270.

38. A. L. Shiguihara, M. A. Bizeto and V. R. L. Constantino, *J. Braz. Chem. Soc.*, 2010, **21**, 1366-1376.

39. J. X. Huang, *Pure Appl. Chem.*, 2006, **78**, 15-27.

40. J. Stejskal, I. Sapurina, M. Trchova and E. N. Konyushenko, *Macromolecules*, 2008, **41**, 3530-3536.

41. R. Abe, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo and K. Domen, *Chem. Mater.*, 1997, **9**, 2179-2184.

42. G. B. Saupe, C. C. Waraksa, H. N. Kim, Y. J. Han, D. M. Kaschak, D. M. Skinner and T. E. Mallouk, *Chem. Mater.*, 2000, **12**, 1556-1562.

43. M. A. Bizeto and V. R. L. Constantino, *Microporous Mesoporous Mater.*, 2005, **83**, 212-218.

44. G. Du, Q. Chen, Y. Yu, S. Zhang, W. Zhou and L.-M. Peng, *J. Mater. Chem.*, 2004, **14**, 1437-1442.

45. Y. Yao, G. S. Chaubey and J. B. Wiley, *J. Am. Chem. Soc.*, 2011, **134**, 2450-2452.

46. J. Goldstein, D. E. Newbury, D. C. Joy, C. E. Lyman, P. Echlin, E. Lifshin, L. Sawyer and J. R. Michael, *Scanning Electron Microscopy and X-ray Microanalysis*, Kluwer Academic/Plenum Publishers, New York, 2003.

47. M. A. Bizeto, F. Leroux, A. L. Shiguihara, M. L. A. Temperini, O. Sala and V. R. L. Constantino, *J. Phys. Chem. Solids*, 2010, **71**, 560-564.

48. M. Mączka, M. Ptak, A. Majchrowski and J. Hanuza, *J. Raman Spectrosc.*, 2011, **42**, 209-213.

49. Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima and T. Kawagoe, *Macromolecules*, 1988, **21**, 1297-1305.

50. G. Louarn, M. Lapkowski, S. Quillard, A. Pron, J. P. Buisson and S. Lefrant, *J. Phys. Chem.*, 1996, **100**, 6998-7006.

51. M. Cochet, G. Louarn, S. Quillard, J. P. Buisson and S. Lefrant, *J. Raman Spectrosc.*, 2000, **31**, 1041-1049.

52. M. I. Boyer, S. Quillard, G. Louarn, G. Froyer and S. Lefrant, *J. Phys. Chem. B*, 2000, **104**, 8952-8961.

53. M. Lapkowski and E. M. Geniés, *J. Electroanal. Chem.*, 1990, **279**, 157-168.

54. J. C. Scott, P. Pfluger, M. T. Krounbi and G. B. Street, *Phys. Rev. B*, 1983, **28**, 2140-2145.

55. A. G. MacDiarmid, J. C. Chiang, A. F. Richter and A. J. Epstein, *Synth. Met.*, 1987, **18**, 285-290.

56. F. Lux, *Polymer*, 1994, **35**, 2915-2936.

57. A. P. Monkman, D. Bloor and G. C. Stevens, *J. Phys. D: Appl. Phys.*, 1990, **23**, 627.

58. S. Bhadra and D. Khastgir, *Polym. Degrad. Stab.*, 2008, **93**, 1094-1099.

59. V. G. Kulkarni, L. D. Campbell and W. R. Mathew, *Synth. Met.*, 1989, **30**, 321-325.

60. T. Hagiwara, M. Yamaura and K. Iwata, *Synth. Met.*, 1988, **25**, 243-252.

61. S. A. Chen and H. T. Lee, *Macromolecules*, 1993, **26**, 3254-3261.

62. J. A. Conklin, S. C. Huang, S. M. Huang, T. L. Wen and R. B. Kaner, *Macromolecules*, 1995, **28**, 6522-6527.

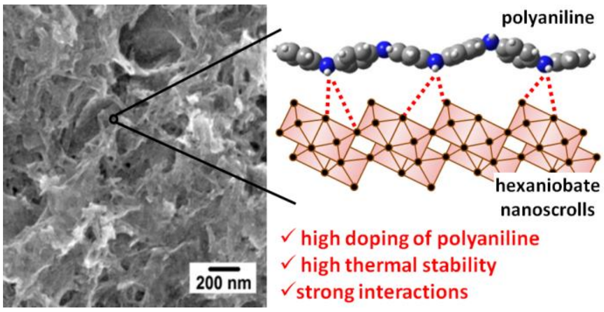
63. M. I. Boyer, S. Quillard, E. Rebourt, G. Louarn, J. P. Buisson, A. Monkman and S. Lefrant, *J. Phys. Chem. B*, 1998, **102**, 7382-7392.

64. M. M. Nobrega, C. H. B. Silva, V. R. L. Constantino and M. L. A. Temperini, *J. Phys. Chem. B*, 2012, **116**, 14191-14200.

65. J. E. P. da Silva, D. L. A. de Faria, S. I. C. de Torresi and M. L. A. Temperini, *Macromolecules*, 2000, **33**, 3077-3083.

66. G. M. do Nascimento, C. H. B. Silva and M. L. A. Temperini, *Polym. Degrad. Stab.*, 2008, **93**, 291-297.

Graphical and textual abstract



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