



## Synthesis and characterization of nanocomposites consisting of polyaniline, chitosan and tin dioxide

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### HIGHLIGHTS

- Nanocomposites of PANI, SnO<sub>2</sub> and chitosan were synthesized by in situ polymerization.
- The structural and thermal properties of powder nanocomposites was investigated.
- Protonation degree of PANI in the nanocomposite with CS is higher than pure PANI.

### ARTICLE INFO

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### ABSTRACT

Polymeric nanocomposites composed of polyaniline (PANI)/tin dioxide (SnO<sub>2</sub>), and PANI/chitosan(CS)/SnO<sub>2</sub> were synthesized chemically by in situ polymerization method. The aniline polymerization was carried out using DBSA as protonating agent, and APS as oxidizing agent. The tin dioxide nanoparticles dissolved in hydrochloric acid (HCl) was added during the synthesis process. Nanocomposites were examined by X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR), photoelectrons excited by X-rays (XPS), and Mössbauer (EM). The results of XRD pattern indicate that nanocomposites are crystalline due to the presence of SnO<sub>2</sub> nanoparticles with reflection planes corresponding to the tetragonal rutile structure. XPS and FTIR results reveal that the protonation degree of PANI/CS/SnO<sub>2</sub> sample is higher than that of the PANI/SnO<sub>2</sub> and pure emeraldine salt PANI samples. These results suggest that the conductivity would be much larger in the PANI/CS/SnO<sub>2</sub> sample. TGA results reveals samples with SnO<sub>2</sub> shows more thermal stability due to Sn<sup>4+</sup> interaction with amide and imide groups of PANI. SEM images of both nanocomposites showed an irregular morphology with agglomerate of particles, attributed to the presence of SnO<sub>2</sub> nanoparticles which were not dispersed homogeneously during the synthesis process.

### 1. Introduction

Conducting polymers have a wide range of potential applications in different technological fields [1–3]. They are present in electronic and electrochromic devices [3,4] and are promising materials in the production of sensors [3,5,6], supercapacitors [7,8], photovoltaic cells [9,10], rechargeable battery [11,12] et al. Among the conducting polymers, polyaniline stands out due to its excellent electrical properties, chemical stability under environmental conditions, easy process synthesis, and low cost [13]. PANI can be used in applications such as electrically conducting yarns [14,15], anticorrosion coatings [16], fuel cells [17], electromagnetic shielding [18]. On the other hand,

researches indicate that the properties and, therefore, the applicability of PANI can be significantly improved by the addition of inorganic nanometre-sized particles of metal, alloys and compounds inside polymeric matrix [19] to form polymer nanocomposites. As a result, new materials – with properties and functionalities different from their components – emerge. Consequently, nanocomposites of PANI and different type of nanoparticles of various size, shape and composition have been studied extensively. The development of polymeric nanocomposites consisting of oxide metal nanoparticles and PANI such as ZnO [20], TiO<sub>2</sub> [21], CeO<sub>2</sub> [22] and SnO<sub>2</sub> [8,23,24] has gained significance due to the improvement of important properties for these materials and their high potentiality in nanotechnological applications.

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In particular, nanocomposites of PANI/SnO<sub>2</sub> synthesized by different routes have been studied extensively in order to be employed in many promising fields including applications in supercapacitors, lithium ion batteries, solar cells and ammonia gas sensors [8,25–28]. It is widely known that the wt% of SnO<sub>2</sub> and its distribution in the polymeric matrix are relevant in the charge transport process of PANI during the synthesis of PANI/SnO<sub>2</sub> nanocomposite using in situ chemical polymerization [29–32]. On the other hand, it has also been reported that SnO<sub>2</sub> and chitosan composites were uniformly distributed over the PANI matrix, resulting in PANI/CS/SnO<sub>2</sub> hybrid composite with improved electrical properties [8]. The chitosan is a natural polymer with outstanding characteristics such as its biocompatibility, biodegradability, non-toxicity and antimicrobial activity, besides its low cost [33,34]. Nanocomposites of CS and metal oxides are multifunctional materials used for applications in adsorption of heavy metal ions [35,36], tissue engineering [37,38], protein adsorption [39], sensors [40–42] et al.

The aim of this research is to obtain PANI/SnO<sub>2</sub> and PANI/CS/SnO<sub>2</sub> nanocomposite powder by employing an in situ chemical polymerization method under the same conditions. The authors also aim to provide a comparative analysis of PANI/SnO<sub>2</sub> and PANI/CS/SnO<sub>2</sub> powder properties. The nanocomposites were characterized using Fourier transform infrared (FTIR), X-ray photoelectrons spectroscopy (XPS), Mössbauer spectroscopy, X-ray diffraction (XRD), thermal gravimetric (TGA), differential scanning calorimetry (DSC) and Scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Materials

Acetic acid (CH<sub>3</sub>COOH), hydrochloric acid (HCl) and acetone (CH<sub>3</sub>COCH<sub>3</sub>) were acquired from VETEC. Aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) and low molecular weight chitosan (CS) were purchased from Sigma-Aldrich. Dodecylbenzenesulfonic acid (DBSA) was purchased from Azul Química, and ammonium persulfate (APS) was acquired from Merk. SnO<sub>2</sub> nanoparticles were obtained by high energy milling using the chemically treated cassiterite, provided by the MELT Mining Industry, as raw material.

### 2.2. Synthesis of PANI, PANI/SnO<sub>2</sub>, PANI/CS and PANI/CS/SnO<sub>2</sub>

PANI was synthesized by the chemical method based on the research of Yu et al. (2011) and Tai et al. (2007), using DBSA as proton doping agent, APS as an oxidizing agent, and aniline as a monomer. APS was dissolved in 40 mL of 0.37 mM HCl in concentration of 16 mM. DBSA was diluted in concentration of 10 mM in the other part of the HCl solution (40 ml). The DBSA solution was kept around 0 °C and under magnetic stirring for 10 min for solution homogenization. After that, aniline in concentration of 27 μM was added to the DBSA solution during continuous stirring. The APS solution was added dropwise [43,44] and the final solution was kept at a temperature around 0 °C for 24 h. Finally, the solution was filtered and washed using deionized water and acetone, and dried at room temperature, resulting in a green powder.

PANI/SnO<sub>2</sub> was prepared dissolving 20, 25 and 30 wt % of SnO<sub>2</sub> in 10 mL of 0.37 mM HCl solution. DBSA was also diluted in HCl solution (30 mL) in concentration of 13 mM. This concentration was performed for posterior corrections of concentration when mixing SnO<sub>2</sub> and DBSA solutions. These solutions were mixed and kept under magnetic stirring for 10 min. The procedures for PANI polymerization were the same as PANI samples, resulting in a PANI/SnO<sub>2</sub> nanocomposite.

PANI/CS blend was synthesized by diluting 0.2 g of chitosan in 0.35 M of acetic acid solution. This solution was kept under magnetic stirring until total biopolymer dissolution [45]. Then, similar PANI polymerization was done adding chitosan solution with 0.5% w/v

concentration during DBSA solution agitation.

The PANI/CS/SnO<sub>2</sub> nanocomposite was obtained diluting 0.34 g of SnO<sub>2</sub> during CS dissolution for 24 h. The same procedures for PANI/CS were carried out to synthesize the nanocomposite. The samples were prepared with 20, 25 and 30 wt % of SnO<sub>2</sub>. The results of all polymerizations were stored in hermetically sealed glass vial.

### 2.3. Characterization

The samples were characterized by Fourier transform infrared spectroscopy (FTIR) using a Irtaffinity-1 Shimadzu spectrometer with a spectral range of 4000–400 cm<sup>-1</sup>. The crystalline structure was analyzed by X-ray diffraction (XRD) using a Philips diffractometer PW-Mark 1710 with CuKα radiation and wavelength of λ = 1.5406 Å operated at 40 mA and 45 kV. Mössbauer spectra (<sup>119</sup>Sn) were obtained using a constant acceleration spectrometer moving a source of BaSnO<sub>3</sub> maintained at room temperature. The spectrum was adjusted assuming computationally simple Lorentzian lines. X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultra-high vacuum environment, with a baseline pressure better than 2.0 × 10<sup>-9</sup> mbar. A monochromatic x-ray source with a power of 350 W was used from an Al Kα target. A SPECS hemispherical electron analyzer model PHOIBOS 150 MCD was also used. The collected spectra were adjusted using the CasaXPS program. For calibration of the spectra, the residual carbon peak with energy of 284.6 eV was used as reference. Scanning electron microscopy (SEM) was performed with the LEO EVO 40 XVP equipment to study the microstructural analysis.

Thermal characterization was analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). For DSC, the DSC-60A of Shimadzu detector with a heating rate of 10 °C min<sup>-1</sup> was used in the range of 30 °C–250 °C. In TGA measurements, the DTG Shimadzu-60AH equipment was used with a heating rate of 10 °C min<sup>-1</sup>, and the samples were heated from 30 °C to 1000 °C under nitrogen atmosphere.

## 3. Results and discussion

### 3.1. Fourier transform infrared spectroscopy (FTIR)

Chitosan (CS), PANI and PANI/CS were characterized by FTIR spectroscopy. The characteristic FTIR bands of CS are shown in Fig. 1(a). The large band between 3500 and 3200 cm<sup>-1</sup> is related to the axial deformation of the O-H group and to the stretching vibration modes of N-H functional groups, whose the bands are overlapped [46,47]. The band between 2955 and 2800 cm<sup>-1</sup> is due to stretching vibration of C-H, related of to the presence of methyl groups in the chitosan structure [48]. In 1657 cm<sup>-1</sup>, it corresponds to the stretching of the C=O bond (axial deformation) of amide [45,48,49]. The bands assigned to the functional groups of secondary and tertiary amide are between 1320 and 1500 cm<sup>-1</sup>. Finally, the region between 1170 and 895 cm<sup>-1</sup> corresponds to the saccharide structure of chitosan [46].

FTIR spectrum for emeraldine salt is presented in Fig. 1(b). The bands 1556 and 1462 cm<sup>-1</sup> correspond to stretches of N = Q = N bonds of quinoid ring (Q) and NH-B-NH of benzenoid ring (B), respectively. The estimation of the relative intensities ratio of band corresponding to these bands (Q/B) of PANI sample was close to one. This last result and the bands indicates the presence of doped polyaniline. The band at 1295 cm<sup>-1</sup> is related to C-N stretch of the secondary aromatic amine of the PANI and a small shoulder at 1230 cm<sup>-1</sup> is attributed to the presence of C-N<sup>+</sup> of the polaronic structure [50,51]. The band at 1126 cm<sup>-1</sup> represents the C-H vibration of N = Q = N and B-N<sup>+</sup>H-B structures, and it is related to the presence of charge carriers along the polymer chain due to protonation process. These charges generate an electron delocalization, which is the evidence the conductive character of the PANI [17,52]. All these results confirm that PANI sample contain the conducting emeraldine salt phase.

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