

## ORIGINAL PAPER

## X-ray absorption spectroscopy of nanostructured polyanilines

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In this paper, X-ray absorption near edge spectroscopy at the nitrogen K edge (N K XANES) data of polyaniline (PANI) and its derivatives were revisited and expanded. The N K XANES spectra of PANI nanocomposites and PANI nanofibers were also investigated. The analysis of N K XANES spectra were done by the deconvolution of bands and the  $1s \rightarrow \pi^*$  and  $1s \rightarrow \sigma^*$  transitions were assigned by a correlation with the N K XANES spectra of smaller organic compounds. The “free” forms of PANI were dominated by bands from 397.7 eV to 399.1 eV attributed to imine and radical cation nitrogen atoms, respectively. Nitrogen bonded to phenazine-like rings can also be seen, mainly for PANI prepared at pH higher than 3.0. The spectra of nanocomposites show sharper bands than the “free” polymers as well as new bands at 398.8 eV and 405–406 eV. These new bands were assigned to phenazine-like rings and azo bonds in the structure of the polymers (polyaniline, polybenzidine, and poly(*p*-phenylenediamine)) within the galleries of the montmorillonite clay. PANI nanofibers doped with HCl or HClO<sub>4</sub> show bands related to phenazine-like rings and/or dication segments of PANI, indicating that these segments are important in the formation of PANI nanofibers.

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## Introduction

Polyaniline (PANI) and its derivatives form one of the largest groups of conducting polymers (MacDiarmid et al., 1987; MacDiarmid & Epstein 1989; MacDiarmid 2001; Trchová et al., 2012). These polymers are frequently prepared by oxidative polymerization in acid aqueous solutions, where no special synthetic conditions are required. The resulting polymer shows high thermal and environmental stability and, depending on the synthetic pathway, a polymer with high solubility can be produced. Recently, the preparation of nanostructured PANI has been introduced in order to improve their properties (Huang & Wan, 1999; Huang & Kaner, 2004a, 2004b; do Nascimento et al., 2002a, 2002b, 2004a, 2006a, 2006b, 2008a, 2008b, 2008c; do Nascimento & Temperini 2006, 2008b). Electronic structure of PANI is strictly related to its oxidation and protonation states. Its structure con-

sists of repeated segments of benzenoid units (reduced rings) and quinoid units (oxidized rings), as shown in Fig. 1. The most common forms of PANI are denominated leucoemeraldine (PANI-LB, for  $y = 1$ , Fig. 1), emeraldine (PANI-EB, for  $y = 0.5$ ), and pernigraniline (PANI-PB, for  $y = 0$ ), corresponding to the different oxidation states of the PANI backbone. The conducting form of PANI is the salt form or protonated PANI-EB known as emeraldine salt of PANI (PANI-ES, Fig. 1).

More recently, spectroscopic techniques that employ electromagnetic radiation of higher energy, ranging from vacuum UV ( $\approx 10\text{--}40$  eV, 125–31 nm), including soft X-rays (40–1500 eV, 31–0.8 nm), and going to hard X-rays (1500– $10^5$  eV, 0.8–0.01 nm) (Margaritondo, 1988; Bilderback et al., 2005; Heald, 1988), has been proven to be of great importance in elucidating molecular structures of chemical and biological interest. In literature, mainly through the work of

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