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SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE NANOTUBES IN THE PRESENCE OF COLLOIDAL TIO_2 NANOPARTICLES

M. Radoičić[1], Z. Šaponjić[1], J. Nedeljković[1], J. Stejskal[2] and G. Ćirić-Marjanović[3]

[1]*Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia*
[2]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic*
[3]*Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11158, Belgrade, Serbia (gordana@ffh.bg.ac.yu)*

Abstract

Conducting polyaniline nanotubes were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in water, in the presence of colloidal TiO_2 nanoparticles of an average diameter ~5 nm. Polyaniline-TiO_2 nanocomposite has been characterized by the electrical conductivity measurements, thermogravimetric analysis, FTIR spectroscopy, scanning and transmission electron microscopies. The electrical conductivity of synthesized nanocomposite was 1.1×10^{-3} S cm^{-1}, slightly higher than that of pure polyaniline prepared under the same conditions. Polyaniline nanotubes have an outer diameter of 45–230 nm nm, an inner diameter of 15–130 nm, and a length extending from 0.5 to 2.0 µm.

Introduction

It has recently been shown that the dispersibility and processability of nanostructured conducting polymers, as well as their performance in numerous applications, are significantly improved in comparison with conducting polymers having granular morphology [1]. The preparation of self-assembled PANI nanotubes and nanorods has received a growing attention during the last years [2–4]. Oxidative polymerization of aniline with ammonium peroxydisulfate (APS) as an oxidant in aqueous solutions (the initial pH $\geq$ 3.5) represents an efficient synthetic route to PANI nanostructures, without the use of an external template [2–4]. In recent years, synthesis of conducting polymer/inorganic particles composites with improved mechanical properties, processability and heat resistance, in comparison to corresponding pure conducting polymer, constitutes an important scientific challenge. TiO_2 nanoparticles are especially interesting because of their unique electrical and optical properties, as well as extensive industrial applications [5]. The hybrid PANI-TiO_2 nanomaterials, which combine the electrical conductivity of PANI and UV-sensitivity of TiO_2, look as a promising candidate for application in electrochromic devices, nonlinear optical systems, and photo electrochemical devices [6]. Although many papers on PANI-TiO_2 nanocomposites have been published [7], only one work was devoted to the preparation of PANI-TiO_2 nanotubes, in the presence of β-naphthalenesulfonic acid [8]. The purpose of this work is the synthesis of conducting PANI nanotubes by the oxidative polymerization of aniline with APS in the presence of colloidal TiO_2 nanoparticles of an average diameter ~5 nm, in aqueous solution without added acid, and characterization of prepared nanocomposite by scanning (SEM) and transmission (TEM) electron microscopies, FTIR spectroscopy, and thermogravimetric (TGA) and electrical conductivity measurements.

Results and Discussion

Colloidal TiO_2 solution, containing nanoparticles of an average diameter ~5 nm, was prepared according to the procedure described by Rajh et al. [9]. In a typical procedure for preparing PANI nanotubes in the presence of TiO_2 nanoparticles, the aqueous solutions of aniline (0.32 M, 25 ml), oxidant (0.4 M APS, 25 ml), and colloidal TiO_2 (0.016 M, 50 ml) were mixed at room temperature. The reaction mixture was stirred for 180 min, and then the precipitated PANI-TiO_2 composite was collected on a filter, rinsed with ethanol acidified with sulfuric acid (5×10^{-3} M), and dried in vacuum at 60 °C for 3 h. As a reference, the pure PANI sample was prepared by the same procedure, without TiO_2 addition.

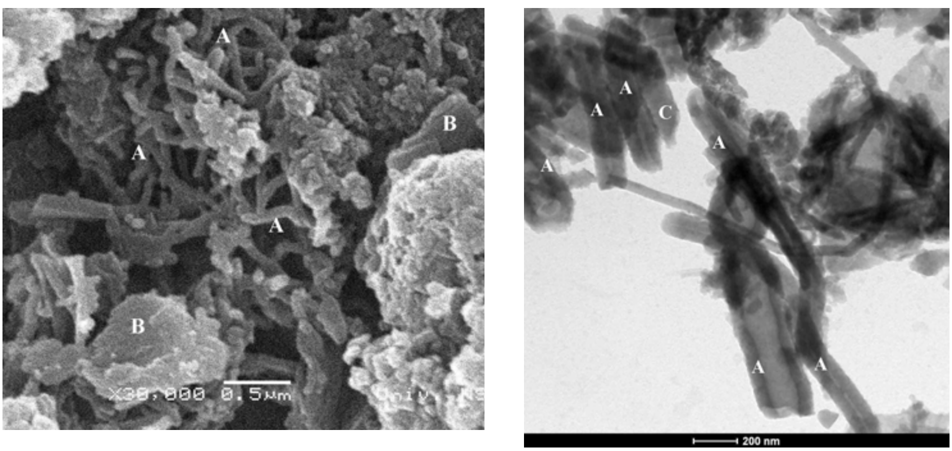

Fig. 1. SEM (left) and TEM (right) images of the PANI-TiO_2 nanocomposite: A-nanotube, B-nanosheet, C-nanorod.

The presence of PANI nanotubes was revealed by SEM and TEM microcopies (Fig. 1, A). Nanotubes have an outer diameter of 45–230 nm, an inner diameter of 15–130 nm, and a length extending from 0.5 to 2.0 µm. The nanotubes are accompanied by nanosheets (Fig. 1, B) and nanorods (Fig. 1, C).

The conductivity of obtained PANI-TiO_2 nanocomposite was 1.1×10^{-3} S cm^{-1}, slightly higher than the conductivity of pure PANI which was synthesized under the same conditions without added TiO_2, 9.1×10^{-4} S cm^{-1}. Figure 2 shows the TGA curves of pure PANI and PANI–TiO_2 nanocomposite, recorded in air stream.

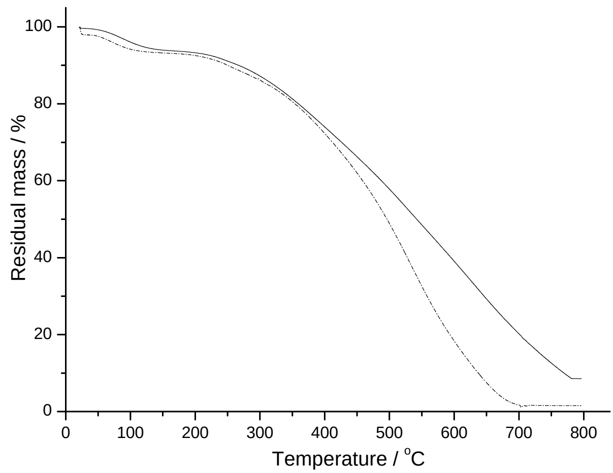

Fig. 2. TGA curves for PANI-TiO_2 nanocomposite (—) and pure PANI (– • –), recorded in air.

In the temperature range 300–780 °C the main weight loss of the PANI-TiO_2 occurred, attributed to the degradation and combustion of PANI backbone. Pure PANI sample was completely decomposed at ca. 700 °C. From the TGA curve obtained during complete combustion of organic matter present in the nanocomposite, the content of TiO_2 in PANI-TiO_2 was determined to amount 8.5 wt. %.

In the FTIR spectrum of PANI-TiO_2 nanocomposite, characteristic bands of PANI were observed at wavenumbers 1569, 1495, 1307, 1246, 1146 and 825 cm^{-1}, as well as the bands of counterions (sulfate and hydrogensulfate) at 617 and 588 cm^{-1}, indicating the presence of PANI chains in its protonated form in PANI-TiO_2.

Conclusion

Conducting PANI nanotubes have been synthesized in the presence of colloidal TiO_2 nanoparticles by the oxidative polymerization of aniline with APS in aqueous solution without added acid. Novel PANI-TiO_2 nanocomposite was characterized by scanning and transmission electron microscopies, FTIR spectroscopy, and thermogravimetric and electrical conductivity measurements.

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