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A new synthesis route to prepare polyaniline (PANI) nanotubes containing magnetic nanoparticles

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Abstract: In this work we report the preparation and characterization of a polyaniline/magnetite (PANI)-Fe_3O_4 nanocomposite, with average diameter around 50 nm and tubular morphology. The tubular nanocomposite was synthesized by an in situ polymerization of aniline using Fe_3O_4 nanoparticles as an oxidant agent. The Fe_3O_4 nanoparticles with narrow size distribution were synthesized by co-precipitation technique and the products were characterized by powder X-ray diffractometry (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Introduction

Polymer-inorganic composites with an organized structure provide a new functional hybrid between organic and inorganic materials [1, 2]. Among these polymers, polyaniline (PANI) has attracted particular interest due to the fact that its electrical properties can be reversibly controlled by changing the oxidation state of the main chain and by protonating the imines nitrogen atoms [1].

A considerable number of articles have been published on the magnetic and conducting polymeric nanocomposites of polyaniline (PANI) as well as polypyrrole composites containing nanoparticles such as TiO_2, ZrO_2, Fe_2O_3, Fe_3O_4 and SnO_2. The properties of these systems are sensitive to the particle size, inter particle interaction, and temperature [3]. Wan et al. studied a series of PANI composites containing nanomagnets prepared by chemical polymerization [4]. Deng et al. reported the preparation of PANI-Fe_3O_4 nanoparticles with core-shell structure via an in situ polymerization of aniline monomer in an aqueous solution, which contains Fe_3O_4 nanoparticles and surfactant NaDS [5]. The reason for that seems to be the fact that they have many potentials applications in electromagnetic interference shielding [6], electrochromics device [7] non-linear optical systems [8].

Since the discovery of carbon nanotubes by Iijima [9], one-dimensional nanostructures of various materials including metal, sulfide, metal oxides, polymer and even composite have been a subject of intense research because of their potential applications in many areas. In recent years, nanostructures of PANI including nanowires, nonorods and nanotubes have been studied extensively. Few reports have studied the 1D nanostructures of PANI containing Fe_3O_4 nanoparticles. Wan et al. developed a self-assembly method to synthesize 1D PANI-Fe_3O_4 nanostructures, however, the content of Fe_3O_4 is small [10]. In the recent work Alam et al [3] synthesized PANI/Fe_3O_4 nanocomposites using ferrofluid to polymerize aniline monomer in solution and found that the polymer structure of the nanocomposite present a porous structure with two phase systems.

In this work, we report the results of a new synthetic route to obtain tubular nanocomposites of PANI/Fe_3O_4 using Fe_3O_4 magnetic nanoparticles as oxidant agent to polymerize aniline monomer solution, the synthesis process was analyzed as a function of the reaction time and the kind of acid used to prepare the solution. In that case no extra oxidant is necessary for the synthetic process, in this method we putt the Fe_3O_4 nanoparticles in contact with the aniline acid solution under UV irradiation and after the respective time we obtained the nanocomposite with tubular nanostructures

precipitation. The products were characterized by powder X-ray diffractometry (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Experimental

Materials

Aniline monomer (Vetec, 99%) was double distilled under reduced pressure and stored at low temperature before use. Iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) (Vetec, 99%), sodium hydroxide (NaOH) (Riedel-de Haën, 99%), nitric acid (HNO_3) (Dinâmica, 65%), were all of analytical reagent grade and used as received.

Synthesis

The magnetic nanoparticles of Fe_3O_4 were obtained from a suspension of $FeSO_4.7H_2O$ under sonication, where a solution of NaOH was added. This mixture was left under ultrasound for 1 h. After that a black magnetic precipitate (Fe_3O_4) was obtained. The precipitate was washed several times with chloride acid solution, centrifuged and then dried under rotaevaporation.

To these nanoparticles a nitrite aniline solution was added, and was left under UV radiation for 1, 2, 3 or 4 h, as the polymerization starts the suspension turned into a dark green which proves the aniline polymerization is taking place. The composite was centrifuged, washed with distilled water, acetonitrile and dried under vacuum.

General Instrumentation

Wide angle X-ray diffraction patterns of the samples were colleted on a Rigaku diffractometer model DMAX 2400, using Cu Kα radiation (=0.15418 nm) at a scanning speed of $0{,}1^0$ s^{-1} in the range of 2 =15-80^0 with a step $0{,}02^0$. The average crystallite size was estimated for the integral intensity of the X-ray diffraction peak (311) using the Scherer equation 1:

$$Tc = k\ l/\alpha\ cosq \qquad (1)$$

where k is the shape factor, l is the X-ray wavelength (0.15418 nm), α is the full width at half-maximum expresses in until of 2 , and is the Bragg angle (0).

The FT-IR spectra of the products were analyzed on a Bruker model IFS-66 in the range of 4000-400 cm^{-1} using KBr pellets.

The morphology was measured by a scanning electron microscope (SEM, JSM-5900, Joel instruments, Japan) and a transmission electron microscope (TEM, Tecnai-FEI).

Results and Discussion

Fig. 1 shows the wide angle X-ray diffraction patterns for the (a) Fe_3O_4 pure, (b) PANI/Fe_3O_4 nanocomposites obtained after 1 hour of UV irradiation, (c) PANI/Fe_3O_4 nanocomposites obtained after 2 hours of UV irradiation, (d) PANI/Fe_3O_4 nanocomposites obtained after 3 hours of UV irradiation, (e) PANI/Fe_3O_4 nanocomposites obtained after 4 hours of UV irradiation and (f) PANI pure. For Fe_3O_4 sample, a single spinel phase structure is assigned with the characteristic reflections of the Fd3m cubic spinel group. Using the Debye-Scherrer equation analysis the average crystallite size (*Tc*) can be estimated to be 25.38 nm.

Fig. 1 (b-e) shows the X-ray diffraction patterns for the composites PANI/Fe_3O_4, synthesized in nitric acid, after UV irradiation for 1, 2, 3 or 4 hours. It is observed that the crystal size diameter decrease with the increase of the interaction time with UV light with the solution. The average crystallite size, *Tc*, for 1, 2, 3 and 4 hours the interaction of interaction with UV light was 24.20;

24.97; 25.15 and 19.91 nm, respectively. After 4 hours it is observed that *Tc* decreases about 6 nm, and a new phase is formed, probably it can assigned as being γ-Fe_2O_3 (JCPDS n^0: 52-1449).

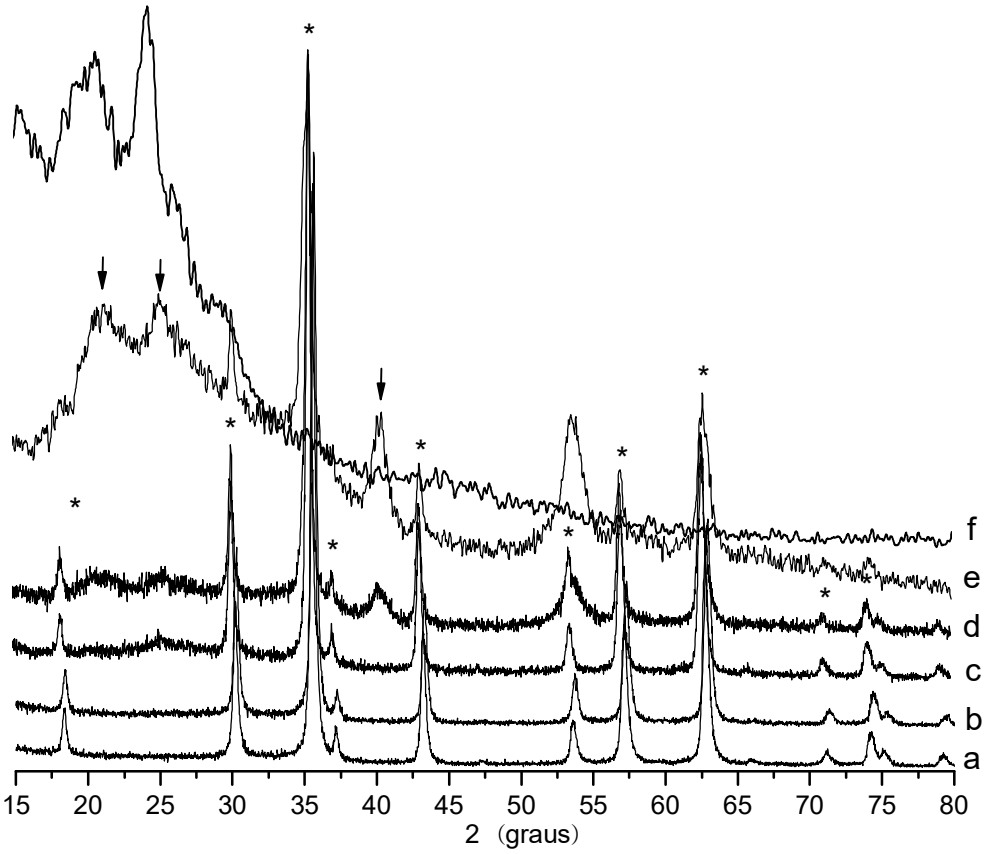

Fig 1: X-ray diffraction patterns for the (a) Fe_3O_4 pure, (b) PANI/Fe_3O_4 nanocomposites obtained after 1 hour of UV irradiation, (c) PANI/Fe_3O_4 nanocomposites obtained after 2 hours of UV irradiation, (d) PANI/Fe_3O_4 nanocomposites obtained after 3 hours of UV irradiation, (e) PANI/Fe_3O_4 nanocomposites obtained after 4 hours of UV irradiation and (f) PANI pure.

The FT-IR spectra analysis for pure magnetite, pure polyaniline and PANI/Fe_3O_4 nanocomposites after 1, 2, 3 and 4 h of UV irradiation are shown in the figure 2. For the spectrum of the pure magnetite a small peak can be observed around 3200 cm^{-1} characteristic of the stretching O-H that can be attributed to the water molecule adsorbed onto the surface of the magnetite nanoparticles, also peaks can be observed around 581, 796 e 889 cm^{-1} which can be attributed to the stretching vibration mode of Fe-O.

For pure PANI (fig. 2) the presence of benzenoid (NH-B-NH) and quinoid (NH-Q-NH) rings vibration is observed at 1500 cm^{-1} and 1574 cm^{-1}, respectively, characterizing the oxidation state of emeraldine salt form of PANI. Two other modes can be observed at 1134 e 1382 cm^{-1} and one mode around 800 cm^{-1} which can be aattributed to the stretching vibration mode C-N and C-H, respectively, this results seems to be in agrement with the literature results for polyaniline in the emeraldine salt form.

For the PANI/Fe_3O_4 nanocomposites we can see that the vibration modes of Fe_3O_4 is shifted to 595, 799 e 877 cm^{-1} and the relative intensity of this mode is changed, characterizing a possibly structure modification during the polymerization process, this results seems to be in agreement with the x-ray measurement where a new phase γ-Fe_2O_3 [**11**], can be observed after 4 hour of synthesis,

also we can observed that a small shift in the polymer mode is observed, indicating a possibly interaction between polymer and the magnetic particles

These results seems to be a strong evidence of the reaction of the Fe_3O_4 nanoparticles with aniline solution in order to form the polymer/Fe_2O_3 nanocomposite particle.

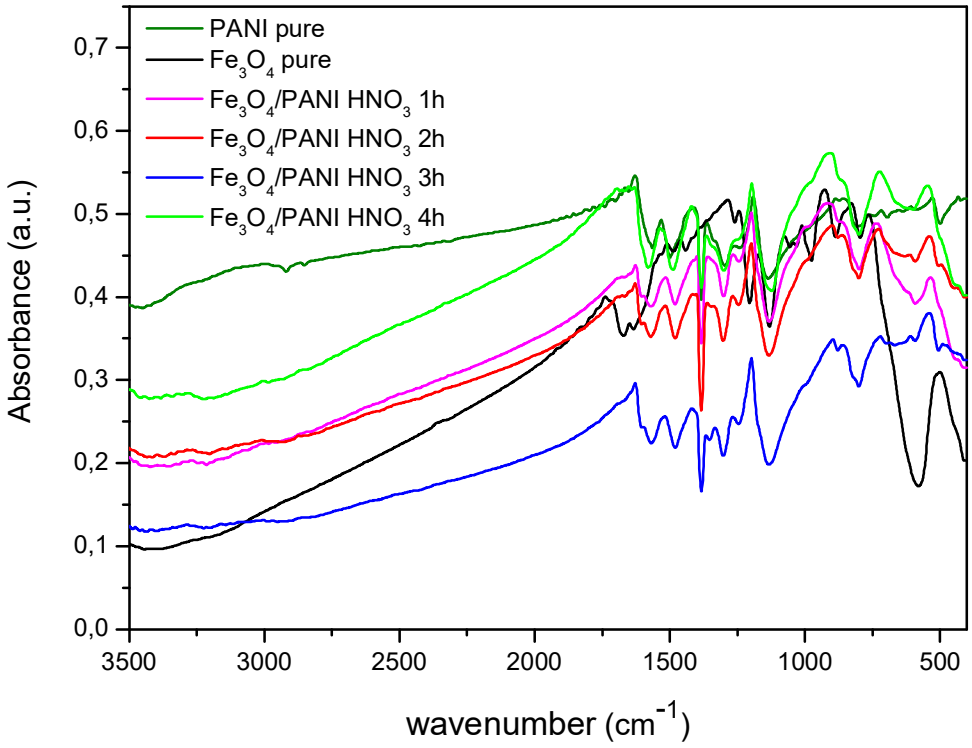

Fig. 2: FTIR spectra of PANI pure, Fe_3O_4 pure and PANI/Fe_3O_4 composite after 1, 2, 3 and 4 h with UV radiation.

Fig. 3 shows the SEM analyses for Fe_3O_4 present a ball like shape with average diameter of 73,05 ± 25,56 nm, indicating that small particle might agglomerate, to form Fe_3O_4 cluster due to magnetic interacting or inter molecular interaction from the X-ray analysis the means diameter of the particles was found to be of the order of 30,97 nm.

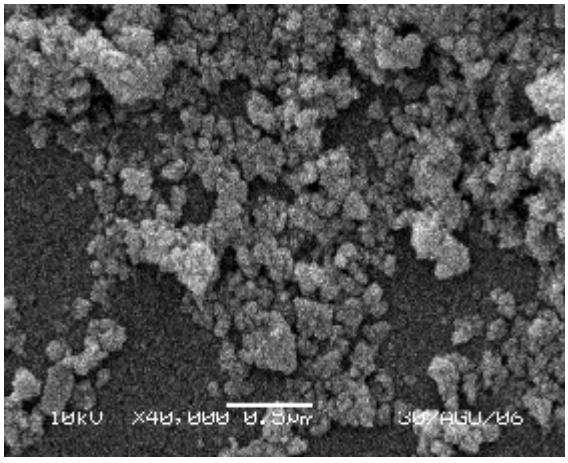

Fig. 3: SEM analysis for the Fe_3O_4 pure.

The SEM images for PANI/Fe_3O_4 (Fig. 4) reveal that the composite presents a fiber shape with mean diameter of the order of 60-80 nm.

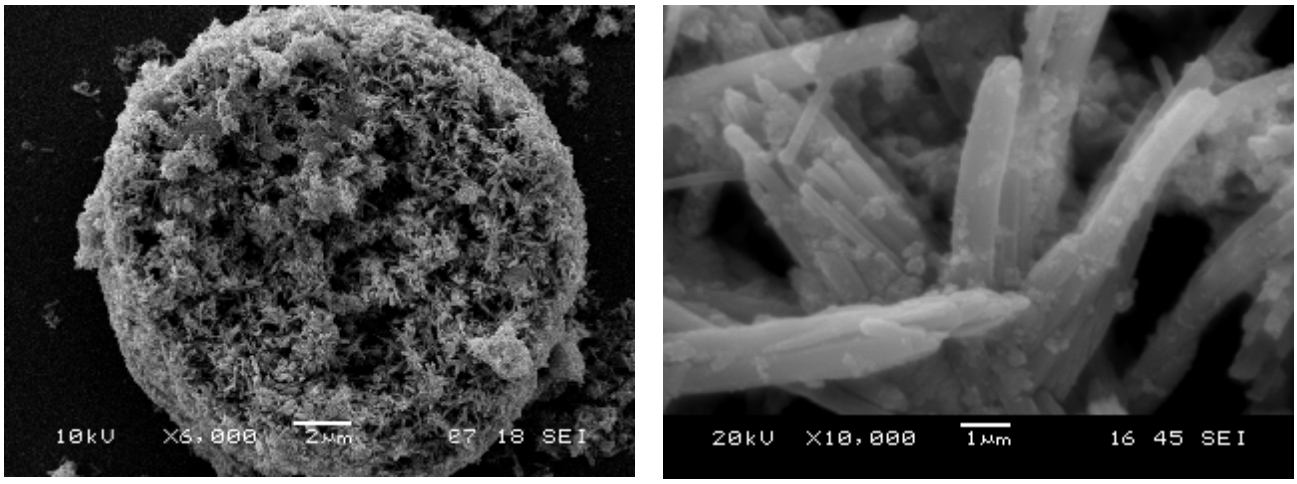

Fig. 4: Micrographies showing tubular morphology.

The TEM images (Fig. 5) suggest this hollow fiber as nanotube, but a small portion of them is solid as nanorod. This results seems to be consistent with Huang et al [12] results for PANI-NSA/Fe_3O_4 composite.

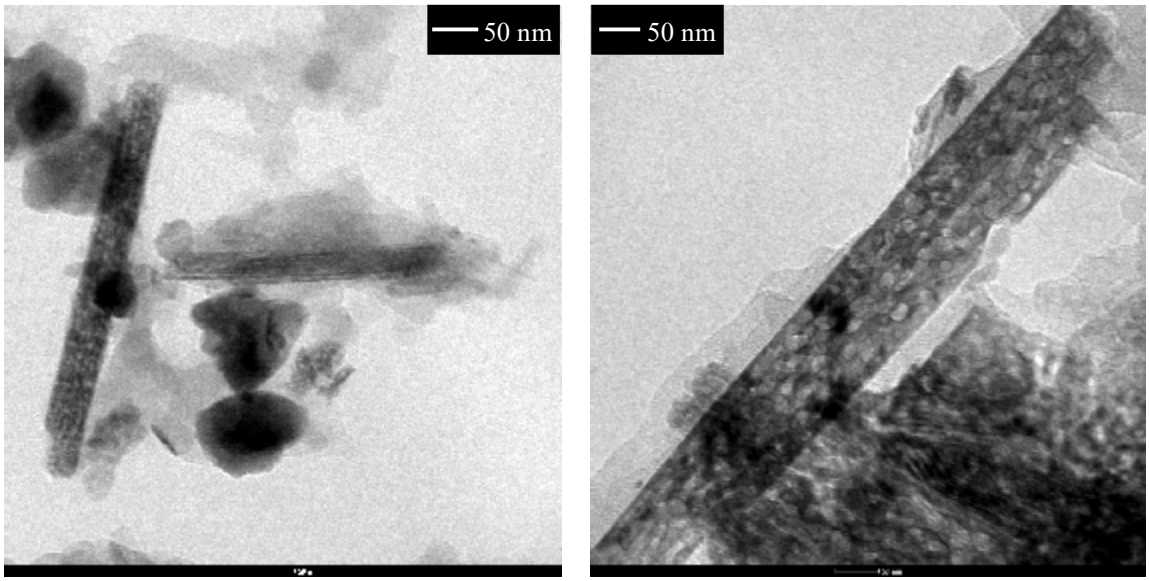

Fig. 5: TEM micrographies showing tubular morphology.

Conclusions

In this work we demonstrated a new method of synthesis of PANI nanofiber containing Fe_3O_4 nanoparticles that act as oxidizing agent for the aniline monomer in the polymerization process, under UV irradiation. SEM and TEM images showed the morphology of the nanofibrous composite and suggested that Fe_3O_4 nanoparticles may be embedded in the composites.

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