



ELABORATION AND CHARACTERIZATION OF CONDUCTING NANOCOMPOSITE INORGANIC/ORGANIC

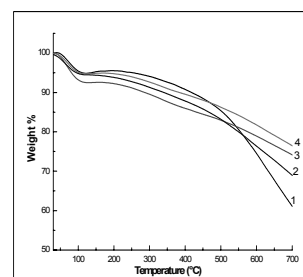
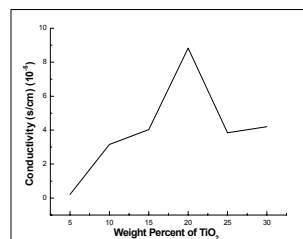
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Conducting polymers such as polyaniline (PANI) present many advantages because their easy synthesis, low cost, tunable doping properties, modifiable electrical conductivity and better stability compared to other polymers. In this study, the hybrid conducting nanocomposite; inorganic/organic was chemically synthesized by in-situ polymerization in aqueous medium within the addition of 50 wt % HY zeolite free acids environmentally friendly, using 5 to 30 wt % of TiO₂ with respect to aniline monomer. The elaborated compounds were characterized by several methods such as: FTIR, XRD, TGA, adding the conductivity measurements. The FTIR spectra indicate the interaction of PANI chains with HY zeolite, and is identical with the interaction between PANI/ HY and TiO₂. The TiO₂ vibrations bands increase with its contents. In comparison to PANI/ HY, the conductivity value increases till 20 wt% of TiO₂, which constitutes the percolation threshold, for the higher contents of TiO₂ the conductivity is still lower and may be due to the partial blockage of conductive path and reduction of conjugation length between PANI chains by excess of TiO₂ nanoparticles within the PANI / HY.



INTRODUCTION*

In the recent years, the development of organic–inorganic nanocomposite materials has grown due to better properties and wide range of uses. These nanocomposites have received greater attention over the last decade because of the interesting possibilities for their structural modifications and promising potential applications in chemistry, biology, medicine and material science. A wide range of organic and inorganic materials can be combined to form nanocomposites with unique electrical, catalytic and optical properties.^{1,2}

In this study, polyaniline was synthesized using 50 w % HY zeolite in the presence of various weight of antase TiO₂ (5–30 w %).

RESULTS AND DISCUSSION

1. FT-IR spectra

Fig. 1 shows the FTIR spectrum of PANI/HY and PANI/HY/TiO₂ nanocomposite, in which some vibration bands are revealed. The characteristic bands attributed to the emeraldine salt were

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3464 cm^{-1} and 3252 cm^{-1} corresponding to stretching vibration of O-H and N-H 38,39, the vibration at 1575 cm^{-1} of quinonoid ring stretching and the band at 1497 cm^{-1} of benzenoid ring stretching are related to vibrations of the C = C of the system (N = Q = N) and system C-C (N-B-N) ring deformation respectively. These two bands are very important and they deliver qualitative information on the oxidation of poly(aniline); the peaks near 2909 cm^{-1} and 2841 cm^{-1} are assigned to stretching vibrations of C-H issued from the PANI structure.^{3,4}

The characteristic bands of the HY zeolite appeared at 1135 cm^{-1} , 1044 cm^{-1} .^{5,6}

The FTIR spectrum confirmed the existence of well defined peaks at the region of 660 cm^{-1} and 505 cm^{-1} due to the group, which are in good agreement with previously reported peaks of TiO_2 the composite,⁷ the maximum peak of TiO_2 occurred in the composite with increase of weight. This means that there is a strong interaction between PANI/HY and TiO_2 .⁸

2. X-ray diffraction (XRD)

Fig. 2 presents the XRD patterns of pure TiO_2 nanoparticles, PANI/HY and PANI/HY/ TiO_2 nanocomposites. It is apparent that the pure TiO_2 nanoparticles are crystalline and the positions of all the sharp peaks reveal that the TiO_2 is in anatase

crystalline form, which corresponds well with PDF#01-071-1168 data file have in good agreement with earlier reported data,⁹ the other crystalline forms TiO_2 *i.e.* rutile and brookite are not detected.

The dominate peaks at 2θ about 25.2149, 36.8268, 37.6676, 38.4568, 47.9658, 53.7731 and 54.9881 represent the indice (101), (103), (004), (112), (200), (105), (211).

The average particle size (D) may be calculated for the selected samples by using Scherrer equation given below:

$$D = K \lambda / \beta \cos \theta$$

where K is the shape factor for the average crystallite (expected shape factor is 0.9), λ is X-ray's wavelength for K_{α} , β is full width at half maximum of the diffraction line, and θ is Bragg's angle.

Adopting the Scherrer formula, the calculated size based on the XDR results, it is estimated that the mean size of TiO_2 nanoparticles is 66.9 nm and nanocomposites content 5% of TiO_2 is 44.6 nm, 10% of TiO_2 is 53.2 nm, 20% of TiO_2 is 55.8 nm, 25% of TiO_2 is 59.9 nm and 30% of TiO_2 is 66.9 nm.

This confirmed that the PANI/HY zeolite/ TiO_2 nanocomposites become more crystalline as the concentration of TiO_2 is increased.

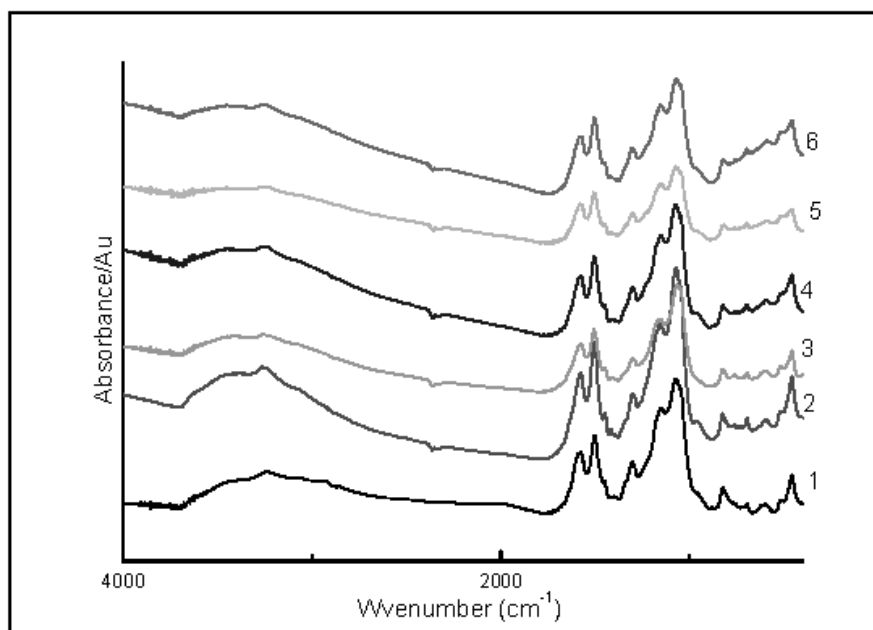


Fig. 1 – FTIR spectra of the 1: PANI/HY zeolite 2: 5 wt %, 3: 10 wt %, 4: 15wt %, 5: 20 wt % and 6: 30 wt % of the PANI/ HY zeolite / TiO_2 nanocomposites.

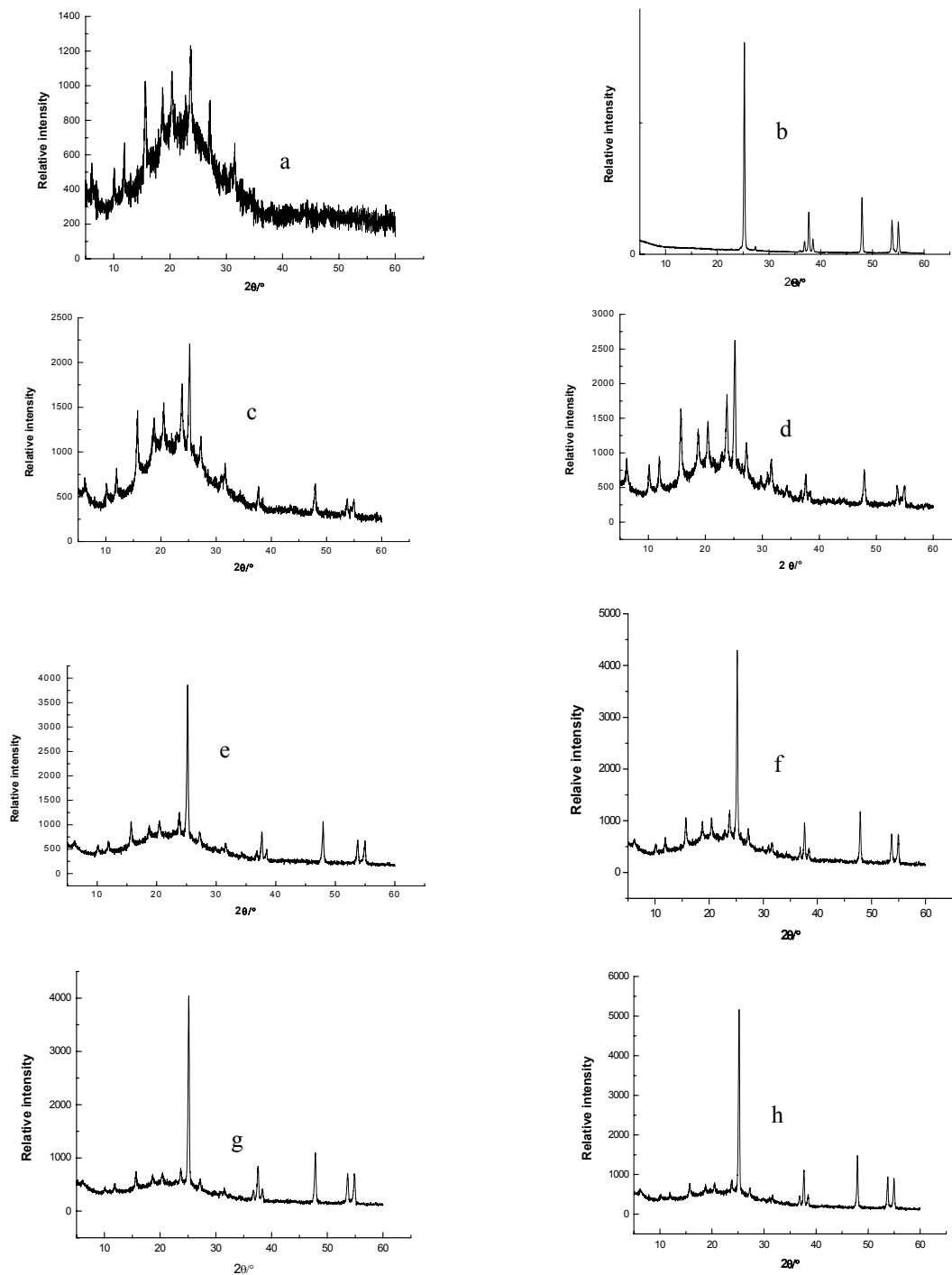


Fig. 2 – The XRD pattern for a: PANI/ HY b: PANI/ HY/TiO₂ c: PANI/ HY/5TiO₂ d: PANI/ HY/10TiO₂ e: PANI/ HY/15TiO₂ f: PANI/ HY/20TiO₂ g: PANI/ HY/25TiO₂ h: PANI/ HY/30TiO₂ nanocomposites.

3. Electrical conductivity

In comparison to pure PANI/HY zeolite the conductivity of 20 wt % PANI/HY zeolite/TiO₂ nanocomposite has been found to have been increased from 5.10^{-4} S/m to $8.83.10^{-3}$ S/m as shown in Fig. 3. This may be attributed to the fact that the doping of TiO₂ nanoparticles within PANI/HY form

a more efficient network for charge transport between different molecular chains of PANI, thus enhancing the conductivity of composite. The decrease in conductivity for 30 wt % PANI/ H/TiO₂ nanocomposite may be due to the partial blockage of conductive path and reduction of conjugation length between PANI/HY chains by excess of TiO₂ nanoparticles within the PANI Zeolite.¹⁰

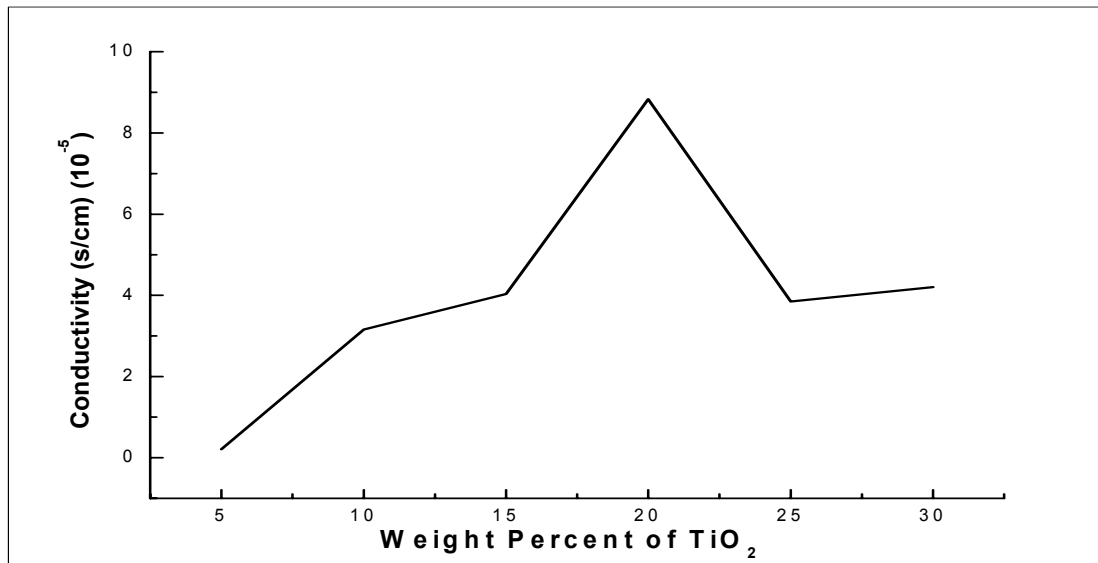


Fig. 3 – Variation in conductivity of PANI/ HY zeolite/TiO₂ nanocomposite with different concentrations of TiO₂ nanoparticles at room temperature.

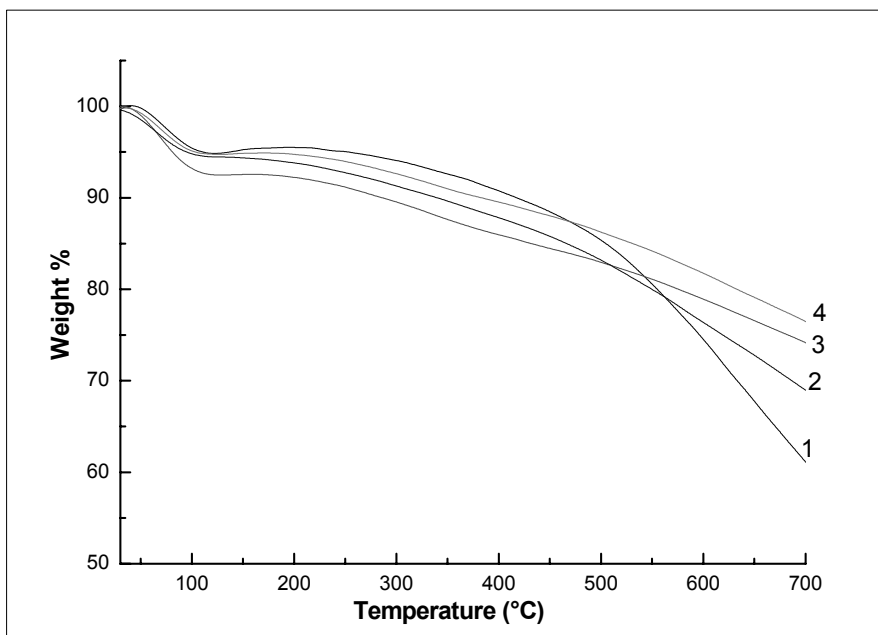


Fig. 4 – TGA curves for 1: PANI/ HY, 2: PANI/ HY /5TiO₂ 3: PANI/ HY/20TiO₂ and 4: PANI/ HY /30TiO₂ recorded in air stream.

4. Thermogravimetric analysis

The thermal stability of PANI/HY and PANI/HY/TiO₂ nanocomposite was evaluated by TGA. Fig. 4 shows the thermogravimetric analysis (TGA) of PANI/HY and PANI/HY/TiO₂ nanocomposites.

For temperature range between 30 and 350 °C we observe an additional weight loss which corresponds to the removal of water molecules in the PANI/HY and PANI/HY /TiO₂ nanocomposites

due to the moisture loss. The noted weight loss at 350-500 °C corresponds to PANI main chain degradation in the PANI/HY and PANI/HY/TiO₂ nanocomposites. This loss is lower than the weight loss in pure PANI. Increased thermal stability of PANI in PANI/HY and PANI/HY/TiO₂ composites can be explained by the strong interaction PANI and HY zeolite, PANI and HY zeolite and TiO₂, which restricts thermal motion of PANI chains.

EXPERIMENTAL

1. Materials

Nanocrystalline TiO₂ (Biochem Chemopharme®), Zeolite NH₄Y [Na₁ (NH₄)₅₂, 33 Al₅₃, 33 Si₁₃₈, 67 O₃₈₄], zeolite international, SiO₂/Al₂O₃ = 5.2; Na₂O = 0.2 %, Si/Al = 2.6 (ZEOLIST®) and chemical reactants: Aniline monomer (Merck®), ammonium peroxodisulfate (NH₄)₂S₂O₈ (Panerac®), ethanol (Merck®) and methanol CH₃OH (AnalaR NORMAPUR®).

2. Preparation of PANI-Zeolite-TiO₂ nanocomposites

The PANI/HY/TiO₂ nanocomposite was prepared by in-situ chemical oxidation polymerization of aniline and HY zeolite using APS as an oxidant in presence of colloidal TiO₂ nanoparticles at 0-5 °C in air. In a typical procedure, the TiO₂ nanoparticles were suspended in distilled water solution and sonicated for 1 h to reduce aggregation of TiO₂ nanoparticles. HY zeolite was dispersed in 25 ml of distilled water, and then 0.1 M of aniline was dissolved in 25 ml of distilled water solution and was poured into the zeolite/aniline (w/w=1) suspension with constant stirring.¹² This suspension was stirred for 30 min, and then mixed with 25 ml of sonicated colloidal TiO₂ nanoparticles by further sonication for 30 min. The 25 ml of distilled water solution containing the APS ((NH₄)₂S₂O₈) with an equal molar ratio to aniline was then slowly added drop wise to the well dispersed suspension mixture for 2 h with a continuous stirring at 0-5 °C. After 3 h, a good degree of polymerization is achieved and the dark green precipitate was recovered. The solution was left in undisturbed position for a night for the completion of chemical reaction. The precipitate produced in the reaction was removed by filtration, washed repeatedly with methanol and distilled water and dried under vacuum for 24 h. The composite powder thus obtained was PANI/HY zeolite and PANI/HY zeolite /TiO₂. The different contents PANI/HY zeolite/TiO₂ nanocomposites were synthesized using 5, 10, 15, 20, 25, 30 wt % of TiO₂ with respect to aniline monomer.

3. Analysis and characterizations

Fourier transform infrared (FT-IR) spectra of the polymers in KBr pellets were recorded on a spectrometer SHMADZU8400S in the absorption mode with 60 scans at a resolution of 1 cm⁻¹ covering the wavelengths between 400 and 4000 cm⁻¹. X-ray diffraction (XRD) was used for the identification of the crystalline phases. The XRD patterns were obtained using a Panalytical Xperpo X-ray diffractometer. They were recorded every 0.02° in the region between 5° and 70°. The thermal stability of sample was performed on a thermogravimetric analyzer (Model: TG 209 F1 NETZSCH German). The electrical conductivity of compressed pellets of the samples is measured using a Four-Point Probe (Jandel Engineering RM3000) with a DC current source, at ambient temperature.

CONCLUSIONS

We have synthesized PANI/ Zeolite TiO₂ nanocomposite with different wt % of TiO₂ by in-situ chemical oxidative polymerization method at low temperature. The electrical conductivity of PANI/Zeolite (HY)/TiO₂ nanocomposite slightly increased with increase in the TiO₂ content upto 20 wt % and then decreased with further additions of TiO₂ in PANI/zeolite. The decrease in conductivity may be due to the partial blockage of conductive path and reduction of conjugation length between PANI chains by excess of TiO₂ nanoparticles within the PANI/Zeolite. The interaction between PANI, HY zeolite and TiO₂ anatase was confirmed by FTIR. XRD of PANI/HY/TiO₂ confirmed the nanometer size range of nanocomposite.

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