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Preparation and Investigation on Structural, Spectral and Electrical Properties of Polyaniline/Manganese Dioxide Nanocomposites

E. Kumar[1*], S.C. Vella durai[2], L. Guru Prasad[3], D. Muthuraj[4], V. Bena Jothy[5]

1. School of Science, Tamil Nadu Open University, Chennai. Tamilnadu, India
2. Department of Physics, JP College of Engineering, Ayikudi, Tenkasi, Tamilnadu, India
3.Department of Science & Humanities, M. Kumarasamy College of Engineering, Karur, India
4. Department of Physics & Research Center, The M.D.T Hindu College, Tirunelveli. Tamilnadu, India
5. Department of Physics & Research Center, Women's Christian College, Nagarcoil. Tamilnadu, India

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Dr. E Kumar
kumarnano@gmail.com
+919600355234

Abstract

Polyaniline/Manganese dioxide (PANI/MnO_2) nanocomposites have been successfully prepared by in-situ polymerization technique. The prepared nanocomposites were characterized by powder XRD, FT-IR, UV and AC impedance spectroscopy. XRD studies reveal that the crystal structure of embedded MnO_2 nanoparticles gets distorted and become amorphous. Vibrational spectra analysis confirms that adsorbed MnO_2 nanoparticles on the surface of polyaniline acts as a compensator for positively MnO_2 nano particles in the formation of PANI/MnO_2 nanocomposites. The absorbance wavelength of PANI/MnO_2 nanocomposites was found from UV spectral analysis. The conductivity nature of the prepared composites was tested using AC impedance spectroscopy. The conductivity of PANI/MnO_2 nanocomposites increased with increase of frequencies dependent.

1. Introduction

Among the available metal oxides, MnO_2 receives much attraction due to its potential application in the field of catalytic and electrochemical applications. The cost of theMnO_2 is relatively cheap compared to other metal oxides and it is available in abundance [1]. Many literatures report that the polymers help to improve the properties of MnO_2 [2-4]. Among the available polymers composites, polyaniline/MnO_2 nanocomposites are used in many applications since the composites capacitance value is significantly enhanced compared to pure MnO_2 [5]. MnO_2 and polyaniline (PANI) receives greater attention due to low cost and Eco friendliness nature [4]. It is reported that the enhancement in specific capacitance happens due to synergistic effect in PANI/MnO_2 nanocomposites. Researchers are paying much attention on PANI due to its promising conducting nature, ease of preparation and good environmental stability. It has many interesting characteristic such as chemical sensitivity and electrochromism. There are many routes are available to synthesis and processing the PANI, among that simple chemical or electrochemical oxidation method is one of the easiest one [6]. The material PANI is widely used in anticorrosion coating, batteries, and sensor [7].

Several reports are available for the preparation of PANI/MnO_2 nanocomposites using an electrochemical method. However, according to our knowledge, no works have been published on the preparation of PANI/MnO_2 nanocomposites via in-situ polymerzation technique with hydrochloric acid and APS as an oxidant. Thus, the present study aimed to prepare PANI/MnO_2 nano-composites using oxidation technique and the subsequent examination of structural, spectral and electrical properties of these nanocomposites. In this manuscript, we report the preparation technique, structural and optical investigation on PANI/MnO_2 nanocomposite.

2. Experimental details

2.1. *Materials*

The AR grade aniline (MERCK) was purchased and distilled twice under reduced pressure. Ammonium persulphate (APS) (Analytical reagent, RANBAXY fine chemicals Limited, India), hydrochloric acid (AR grade

MERCK) and Manganese (II) sulphate (AR grade MERCK), Manganese oxalate (AR grade MERCK] and sodium hydroxide (AR grade MERCK) were also used to prepare the nanocomposites.

2.2. *Synthesis of* MnO_2 *nanoparticles*

The microwave-assisted solution method has been performed by using maganese of two different salts which are manganese (II) sulphate and manganese oxalate. Both salts have different concentration i.e., manganese (II) sulphate and manganese oxalate are mixed with continuous rousing at the temperature of 40°C at one hour. While stirring, NaOH solution was added till the pH of the solution become 12. Then the solution was kept in microwave oven (900W, 2450MHz, Ondia, India) at a temperature of 30°C for about 30min and kept out two hours for cooling. After two hours brown precipitate (MnO_2) were obtained. This was filtered out and washed with deionized water and ethanol. It was dried for three days at room temperature.

2.3. *Synthesis of polyaniline (PANI)*

PANI has been prepared as follows: 4.5 ml aniline was injected into 70 ml of 2M of hydrochloric acid. APS solution was prepared by dissolving 4.5 g of APS in 20ml of deionized water and it was plunged in the aniline solution with steady stirring of about 30 min. This was kept at 40 °C in undisturbed manner for 3 hours for getting polymerization. After that, this mixture was filtered under gravity, and washed with HCl (2M), deionized water and after that it was allowed to dry at 90^0C for one day in vacuum to obtain a fine tint of green powders.

2.4. *Synthesis of PANI/* MnO_2 *nanocomposites*

One weight percentage of PANI/MnO_2 nanocomposites has been prepared as follows: Aniline solution (4.5 ml) and 2 M HCl solution (70 ml) were mixed and stirred at constant temperature. In this mixture, 0.09 g (1%) prepared MnO_2 was added, in order to avoid aggregation, this was stirred upto 6 hrs. After 6 hrs of stirring, APS solution was introduced into drop-wise at 40°C. The reaction mixture was filtered under gravity, and washed with 2M HCl and de-ionized water, afterward dried at 90^0C for one day in vacuum to obtain a fine tint of green powder.

2.5. *Characterisation of PANI,* MnO_2 *and PANI/*MnO_2

The Powder XRD pattern of the prepared materials were recorded using the XPERT-PRO diffractometer with CuKα1 radiation (λ=0.15406 nm). The powder sample was scattered over the angle range of 2θ values (10^0 - 80^0). The FT-IR spectrum was recorded using JASCO FTIR-4100 spectrometer in the wavelength of 400-4000 cm^{-1}. The optical spectrum was traced using UV-2600 spectrometer in the range of 200-1200 cm^{-1}. AC impedance spectroscopic analysis was performed using a computer controlled Zahnner zennium IM6 meter within the frequency range 10 μHz to 8 MHz at different temperatures.

3. Resulats and Discussion

3.1. XRD Studies

Figure 1 shows the XRD patterns of pure MnO_2 particles, pure polyanline and PANI/MnO_2 nanocomposites (one weight percentage). XRD pattern of pure MnO_2 suggests that the materials crystallizes with good crystallinity [8]. The peaks observed at 25°, 28°, 36°, 39°, 42°, 50° and 11°, 22°, 28°, 33° are the characteristics peak of pure MnO_2 nanoparticles and pure PANI . The peaks corresponded to the (2 2 0), (3 1 0), (4 0 0), (3 3 0), (3 0 1) and (4 1 1) of a tetragonal structure of pure MnO_2 nanoparticles and it is identified using standard data JCPDS no.44-0141. The obtained values are in good agreement with the reported values [8]. The unit cell parameters of the Pure MnO_2 sample was observed values by a=9.7847Å,b=9.7847Å and c=2.8630Å and a = b = c = 90^0 [10].

Reported average crystallite size of pure manganese dioxide nanoparticle is around 24 nm [9]. In the present study, the average particle size has been calculated using the Scherer formula given by

$$D = \frac{0.94\lambda}{\beta Cos\theta}$$

Where λ is the wavelength of the X-ray source, β the full width at half maximum, and θ the diffraction angle, the average crystalline size of MnO_2 nanoparticle is found as 20 nm.

The XRD pattern of pure PANI is presented in Figure 1b. It has clearly shown that PANI has partly crystalline nature and the intense peak observed at 25^0 and the same is observed in the XRD of pure PANI. The PANI displayed in a wide peak at 2θ from 14^0 to 32^0 is reported as the characteristic distance between the ring planes of benzene ring in adjacent chain. The broad peak of PANI due to the ring planes of benzene is noticed as a higher background in the region 18^0–35^0 and it has some degree of crystallinity. An intense peak, which is around 25^0 for PANI, should be assigned to the scattering from the periodicity perpendicular to PANI chains.Figure 1c shows the XRD pattern of PANI/ MnO_2 (at one weight percentage) nanocomposites providing the proof for the existence of MnO_2 nanoparticles in the prepared composites, whereas some peaks confirms the amorphous nature of the prepared material (Fig. 1c). This confirms that the PANI/ MnO_2 nanocomposite crystallinity increases by increasing the concentration of MnO_2. This can be observed in Figure 1.d&e.

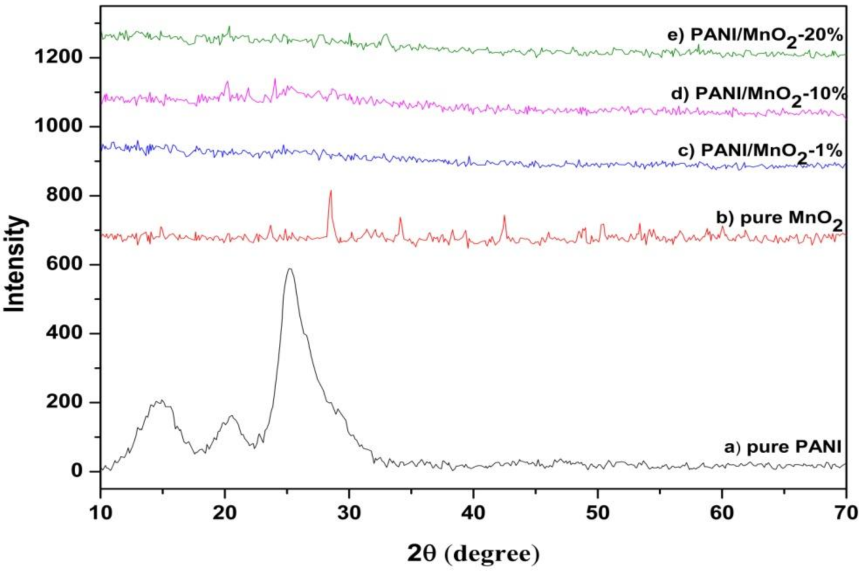

Figure 1: XRD of a) pure PANI b) pure MnO_2 and c,d,e) one, ten and twenty weight percentage of PANI / MnO_2 nanocomposites.

3.2. FTIR Spectroscopy

Vibrational characteristic of the prepared materials were investigated by analysing the FTIR spectrum. The recorded FTIR spectrum of PANI, pure MnO_2 and PANI/MnO_2 is shown in Figure 2. Generally, the Mn-O bending vibrations trace its characteristic peak in the region of 500 cm^{-1} to 900 cm^{-1} [11-13]. Three peaks are observed 768, 810 and 907 cm-1 in the pure MnO_2 sample and are assigned to bending vibration of MnO_2 whereas the same is observed in PANI/MnO_2 at 652 cm^{-1}. Shift towards the lower frequency region of bending vibration confirms the interaction happens between the nanoparticle and the polymer matrix. In the present work, the MnO_2 nanoparticles show broad peak at 3456 cm^{-1} and arises due to the association of adsorbed water molecule. PANI/MnO_2 nanocomposites recorded a vibration peak at 1295 cm^{-1} which takes place due to mixing of benzenoid deformations in PANI and CN stretching. This peak also confirms the occurrence of protonation in CH group of PANI [14].

The peak observed at 1472 cm^{-1} and at 1617 cm^{-1} confirms the presence of benzoid and quinoid ring vibrations which also indicates the oxidation state of emaraldine salt of PANI. The interaction between the metal oxide and the PANI leads charge transfer this can be observed by comparing the intensity of benzoid and quinoid ring vibrational peaks. In pure PANI, the vibraional peak of benzoid peak is large compare to quinoid whereas in the FTIR spectrum of composites shows intensity of quinoid peak is high, this confirm the presence of MnO_2 in the prepared nanocomposites. The small curve observed at 1132 cm^{-1} is the characteristic peak of PANI and which gives information about the degree of delocalization of electrons in PANI. Very weak and broad band curve recorded at 2919 cm^{-1} is consigned to the N–H stretching vibrations. Figure 2 clearly picturises the difference in the vibrational characteristic of functional presented in PANI, pure and PANI/MnO2 sample. The N–H stretching vibration is observed as a broad (weak) curve near to 3000 cm^{-1}. The interaction between MnO_2 and PANI may result in charge transfer activity; difference that can be observed is the intensity ratio of the benzoid and quinoid rings [15].

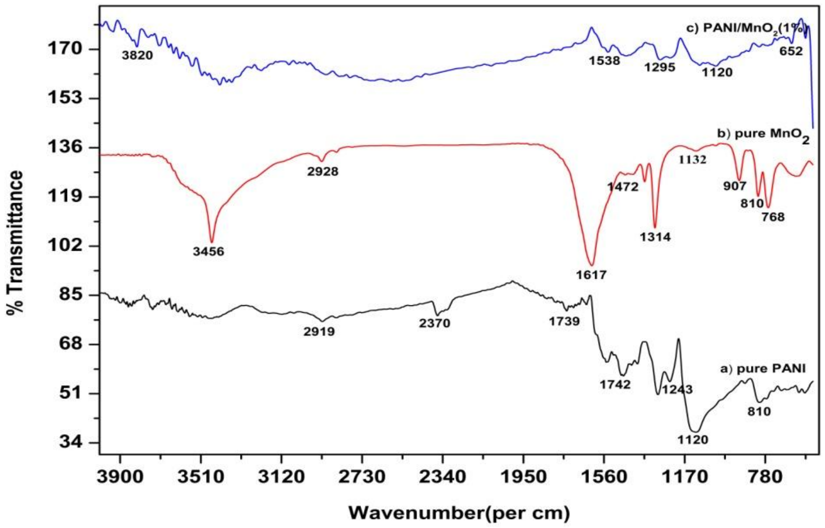

Figure 2: FTIR spectra of a) pure PANI, b) pure MnO_2, and c) PANI / MnO_2

3.3. UV - Visible Spectroscopy

The room temperature ultraviolet-visible spectrum of Pure MnO_2 & PANI, PANI/MnO_2 nanocomposites samples are recorded and are shown in Figure 3. In PANI, an absorption peak observed at 280 nm occurs due to $\pi-\pi*$ transition. In the nanocomposites, this is observed at 427nm as n–$\pi*$. The shift to higher wavelength region clearly indicates the interaction between metal oxide and PANI happens through quinoid because $\pi-\pi*$ in the quinod ring requires less energy [15]. It is also observed that the prepared composites has less transparency nature in the entire UV and visible.

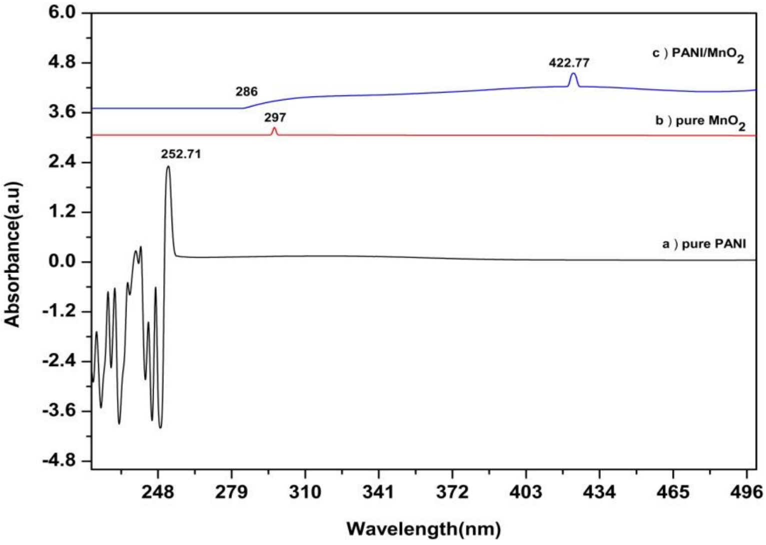

Figure 3: UV-Visible spectra of a) pure PANI, b) pure MnO_2, and c) PANI / MnO_2 nanocomposites.

3.4. Conductivity Analysis

Analysis of AC impedance is a powerful method to characterize the electrical properties of the materials. AC conductivity analysis helps to separate the individual contribution of bulk and interfacial polarization of the samples. Figure 4, 5, 6 shows the frequency dependent conductivity of MnO_2, pure PANI and PANI/MnO_2 nanocomposites at different temperature.

The ac conductivity (σ_{ac}) was computed by using the following formula

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega$$

Here, ε_0 and ω are the permittivity of free space and the angular frequency.

In PANI/MnO_2, conducts the alternating current due to the hopping mechanism. The mathematical form of frequency dependent conductivity can be written as

$$\sigma(\omega) = B(T)\omega(T)^3$$

Figures 4-6 are clearly indicate that the AC conductivity is frequency dependent and are enhanced with increase in the frequency. At low frequency region, the value of conductivity remains constant and it increase by increasing the frequency at high frequency region. It is visible from the Figure 4-6 that the increase in temperature also increases the conductivity and confirms the semiconductor nature of the prepared material. Oxidization of polymer produces the radical cation and the delocalization of charge is not occurs completely in the polymer and it occurs only in the monomers. Radical cation with lattice distortion in the region of the charge is known as polaron and the polaron movement yields increase in conductivity. Formation of bipolarons occurs due to the removal of second unpaired electron from the chain which has a polaron. Deu to the movement of these polaran an increase in conductivity observed at high frequency region. This confirms the charge transport nature of the prepared material. While we increase the temperature above the 398 K it is observed that the conductivity of the prepared PANI/MnO_2 decrease and this occurs due to increase in tunneling of the charge carriers.

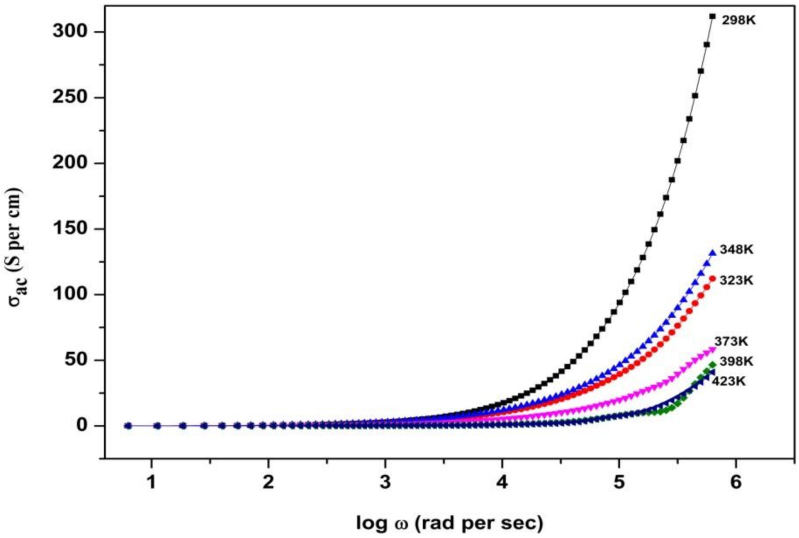

Figure 4: Conductivity spectra for of manganese dioxide at different temperature.

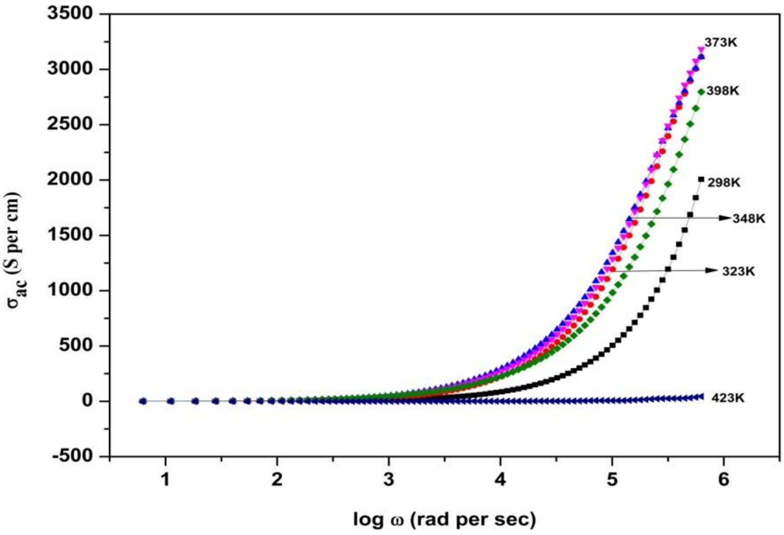

Figure 5: Conductivity spectra for of pure PANI at different temperature

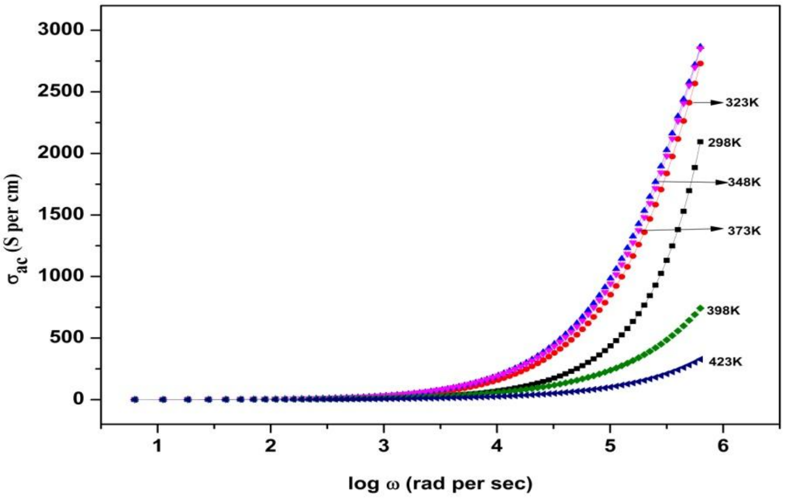

Figure 6: Conductivity spectra for of PANI/MnO_2 nanocomposites at different temperature.

It is visible from the Figure 6 that, at low frequency region, the sample has non-zero value of conductivity for all the operating temperature. The conductivity value of prepared sample is varies in order of 0.31268 to 2865.8837 mho m^{-1}. The conductivity of PANI/MnO_2 nanocomposities has been decreased compare to pure PANI and MnO_2 nanoparticles.

Conclusions

PANI/MnO_2 nanocomposites have been synthesized via in-situ polymerization method and the prepared samples were characterized by varies studies. XRD studies reveal the average crystalline structure of PANI/MnO_2 nanocomposites. The functional groups of the PANI/MnO_2 nanocomposities were identified from FT-IR spectrum. The interaction between the metal oxide and the polymer has been studied by analyzing the absorption spectrum. The conductivity of dielectric spectra analysis of the prepared PANI/MnO_2 nanocomposites has been studied using AC impedance spectroscopy.

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