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Structural, Optical, and AC Conductivity Properties of Polyaniline/Manganese dioxide nanocomposites via In Situ Polymerization

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Abstract- Polyaniline/Manganese dioxide (PANI/MnO_2) nanocomposites were successfully prepared in ten and fifty weight percentage by in situ polymerization. As nanocomposite were characterized by powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Ultraviolet-Visible Spectroscopy (UV), and AC Impedance Spectroscopy. It is revealed by XRD measurements of PANI/MnO_2 nanocomposites that takes place a distortion of crystal structure incorporated of MnO_2 nanoparticles. And it is converted into crystal nature. Ten weight percentage and fifty weight percentage prepared nanocomposites crystalline sizes are 18 nm and 42 nm. FTIR spectra were confirmed by functional group and provide the information about the peaks.The absorbance wavelength of nanocomposites was found from UV- visible studies. The electrical conductivity studies were carried out by Impedance spectroscopy at constant temperature. The electrical conductivity of nanocomposites has been increasing when the frequency was increased.

Index Terms- Nanocomposite, Frequency, Conductivity, Temperature

1. INTRODUCTION

All metal oxides show very good potential applications and it is cheap. There are some chemical applications. They, as the technological importance of manganese oxide, have long been used. An electrochemical super capacitance, however, is exhibited by MnO_2 in comparison with another oxidation [1, 2]. Using MnO_2 and conducting polymer, the nanocomposites is prepared in order to increase the performance of manganese dioxide [3, 4]. Preparation and studies of PANI/MnO_2 nanocomposites are given much attention due it is environmental friendliness. This attention is also due to a coating layer to restrain MnO_2 from dissolution in the acidic environment. PANI is prepared using many methods [5]. PANI is used in anti-corrosion coating, sensors, and batteries [7]. Many research article say that PANI/MnO_2 nanocomposites is prepared using electrochemical method. As per the knowledge of my research, few works have been published so far. So ten and fifty weight percentage nanocomposites (Polyaniline/Manganese dioxide) were prepared via in situ polymerization method, it is with HCl and Ammonium persulphate as the oxidant. Under these circumstances, it is worthwhile to conduct an explorative/investigation on preparing the samples by oxidation method. The initial work is described in this paper. It is utilized for structural, optical, and conductivity study of PANI/MnO_2 nanocomposites

2. MATERIALS AND METHODS

2.1. *Materials*

The chemicals, used in this work, are aniline, ammonium persulphate, HCl, $MgSO_4$, MnC_2O_4, NaOH, and deionized water. To prepare nanoparticles and nanocomposites, these chemicals where used. The above mentioned chemicals and ammonium persulphate were purchased by MERCK (AR grade) and RANBAXY (AR grade).

2.2. *Synthesis of PANI/MnO_2 Composites*

The MnO_2 nanoparticle, using the materials like $MnSo_4$, MnC_2O_4, and NaOH, was prepared by the microwave-assisted solution method. The PANI Nanoparticles, using the materials like polyaniline, ammonium persulphate, and de-ionized water, was prepared by in situ polymerization. Then two different beakers are used in this method, the beakers

contain a mixture of 70 ml of HCl (2M) and 0.98g of MnO_2 nanoparticles. Another beaker contains a mixture of 70 ml of HCl and 4.5g of MnO_2 nanoparticles. The aniline (4.5 ml) was injected in drop vise in each reaction solutions when those beakers are stirred at 40^0C. The prepared two solutions after 6hour, The 4.5 g of ammonium persulphate was mixed in two different 20ml deionized water and solution was prepared. This solution is mixed drop by drop with prepared solution which being stirred. The solution is stirred for three hours. It is kept at 100^0C for two days in vacuum with a view to obtain a green powder finally.

2.3. *Experimental*

Using X-ray diffractrometer (XPERT-PRO using CuKα1, λ=1.540 nm radiations), the prepared nanoparticles and nanocomposites are analyzed. The scattered angle of the above said analysis is 10^0 to 80^0 (2θ values). Using Fourier Transform Infra-Red spectroscopy (FTIR) (JASCO FTIR-4100), the functional group of prepared nanoparticles and nanocomposites were found. The wavelength of the above said analysis is 399.1927-4000.6047cm^{-1}. The sample, using UV Visible spectroscopy (UV-2600), was recorded by absorption. While it is recorded, wave number is 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. RESULTS AND DISCUSSION

3.1. *XRD Studies*

XRD pattern of PANI, MnO_2, and ten & fifty weight percentage of PANI/MnO_2 shows in Figure. 1. It is clear from the beak of figure 1 that the crystalline nature of PANI and MnO_2 Nanoparticles is good. The beaks of PANI and MnO_2 nanoparticles in the figure matches with the original JCPDS are 53-1717 and 44-0141. The particle size of nanoparticles can be calculated by scherrer formula. The scherrer formula d = 0.94λ/βcosθ. The calculated grain size of MnO_2 is around 20 nm and it was confirmed by some articles [8]. The grain size of PANI is around 4 to 9 nm from some articles [9, 10]. The particles sizes of nanocomposites are varying when they are compared with pure MnO_2 and pure PANI nanoparticles. The particles sizes of nanocomposites are small when the MnO_2 concentration is low. It is big when the concentration of MnO_2 nanoparticles is high. The reason is that MnO_2 nanoparticles sit in the PANI surfaces. It is understood from the peak of figure 1. The ten and fifty weight percentage of nanocomposites, which are the particles size 18 nm and 42 nm, were calculated by scherrer formula.

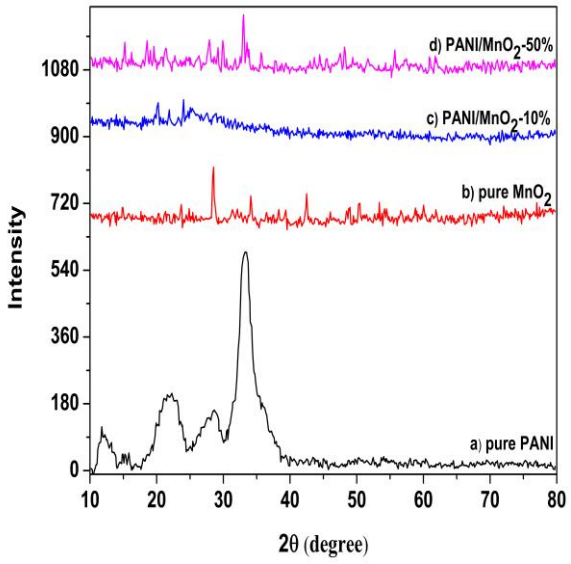

Fig. 1. XRD pattern of a) pure PANI b) pure MnO_2 and c,d,) ten and fifty weight percentage of PANI / MnO_2 nanocomposites.

3.2. *FTIR Spectroscopy studies*

An FTIR spectrum of PANI, MnO2, and 10 & 50 wt% of PANI/MnO_2 nanocomposites shows in Figure. 2. The PANI peaks at 3474, 2923, 2368, 1473, 1301, 1114 and 8073 cm^{-1} are shown in Figure 2a. The MnO_2 peaks at 3456, 2922, 1612, 1365, 1311, 910, 816 and 768 cm^{-1} are shown in Figure 2b. The 10wt% PANI/MnO_2 nanocomposites peaks at 2863, 2534, 2033, 1207, and 901 cm^{-1} are shown in Figure 2c. The 50wt% PANI/MnO_2 nanocomposites peaks at 2870, 2537, 2033, and 901 cm^{-1} are shown in Figure 2d. The peaks 3474 cm^{-1} at N–H stretching mode vibration, 2923 cm^{-1} at N–H in the benzenoid ring, 1743 cm^{-1} at C– C stretching mode for the benzenoid rings, and 1301 cm^{-1} at N-H bending and C–N stretchingmode for the benzenoid ring are clearly shows in PANI. The peaks 3456 and 2922 cm^{-1} at O–H stretching vibration, 1612 cm^{-1} at adsorption of water moisture, 1365 and 1311 cm^{-1} at bending vibration of O-H bonds connected with Mn atoms, and Bending vibration of O-H bonds connected with Mn atoms at Mn-O stretching mode in tetrahedral sites are clearly shown

in pure MnO_2 nanoparticles [11,12,13]. The peaks 2863 cm^{-1} at N–H in benzenoid ring, 1207 cm^{-1} at the C–N stretching of the secondary aromatic amine, and 901 cm^{-1} at Mn-O stretching mode in tetrahedral sites are clearly shows in 10wt% of nanocomposites. The peaks 2870 cm^{-1} at N–H in benzenoid ring, and 901 cm^{-1} at Mn-O stretching mode in tetrahedral sites are clearly shows in 10wt% of nanocomposites. In Figure 2c, 2d clearly shows the 10 and 50 wt % of nanocomposites were compared to PANI and MnO_2.

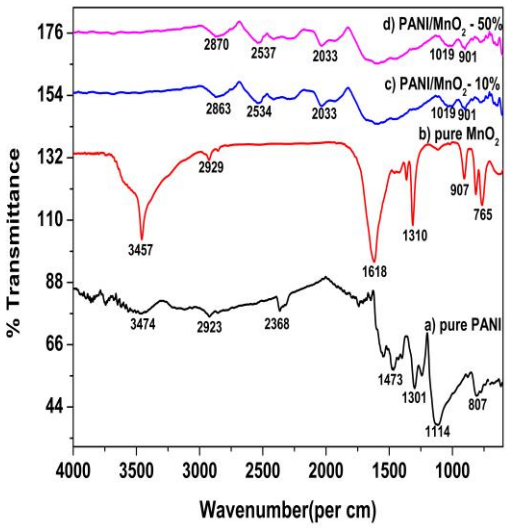

Fig. 2. FTIR spectra of a) pure PANI, b) pure MnO_2, and c,d) ten and fifty weight percentage of PANI / MnO_2 nanocomposites.

3.3. *UV Visible Spectroscopy studies*

UV Visible spectral diagram and an absorption wavelength of PANI, MnO_2, and ten & fifty wt% of nanocomposites are shown in Figure. 3. The UV-visible spectra of pure PANI, pure MnO_2, 10 and 50 wt% of Polyaniline/Manganese dioxide nanocomposites were recorded wavelength of absorption. The around 251 nm for pure PANI in peak, 297 for MnO_2, 244 and 234 for ten and fifty wt% of nanocomposites represents the orbital electron transition $\pi-\pi*$[16]. The polaron–$\pi*$ transition of the chains (PANI) shifted to a lower wavelength side. For absorption wavelength with the presence of nanocomposites, the change was started at 244 and 234 nm. The maximum blue-shifted to 244 nm for 10 wt% of nanocomposites, the minimum blue shifted up to 234 nm for 50 wt% of nanocomposites, compared to 294 nm and 251 nm of MnO_2 nanoparticles and PANI. The $\pi-\pi*$ transition of the aromatic structure has been the presence in 50wt% of nanocomposites, it was confirmed by the strong peak 234 nm [17]. The decreased absorption can be explained by the increase in scattering of light due to the presence of smaller particles. The blue-shift of the absorption minimum from 251 nm in PANI to 244 and 234 nm in 10 and 50wt% of PANI/ MnO_2 nanocomposites is most likely caused by the dopant.

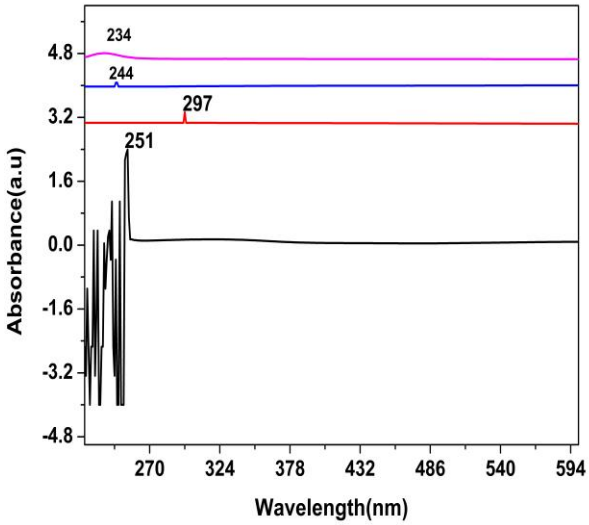

Fig. 3. UV-Visible spectra of a) pure PANI, b) pure MnO_2, and c,d) ten and fifty weight percentage of PANI / MnO_2 nanocomposites.

3.4. *AC Electrical studies*

AC impedance spectral of pure PANI, pure MnO_2, and ten & fifty wt% of nanocomposites at constant temperature (150^0C) shows in Figure. 4. In ten and fifty weigh percentage of PANI/MnO_2 nanocomposites, conducts the AC current due to the hopping mechanism. Figure 4 are clearly indicates that, AC conductivity is frequency dependent and are enhanced with the increase in the frequency. The conductivity remains constant for PANI, MnO_2, 10 and 50 wt% of nanocomposites in the low-frequency region. Conductivity will increase when the frequency increasing at the high-frequency region of PANI, MnO_2, 10 and 50 wt% of nanocomposites. The maximum conductivity of, pure PANI is 43 S per cm, MnO_2 is 40 S per cm, 10 wt% nanocomposites is 134 S per cm and 50 wt% nanocomposites is 553 S per cm. It is clear from the Figure 4, the conductivity of, 10 wt% of PANI/MnO_2 nanocomposites increases at low-frequency region and 50 wt% of PANI/MnO_2 nanocomposites increases in the high-frequency region. The conductivity of PANI/MnO_2 nanocomposites (10 wt% and 50 wt%) are high for the high-frequency region and constant for low-frequency region. The compared to pure nanoparticles, the conductivity of nanocomposites are low for the high-frequency region.

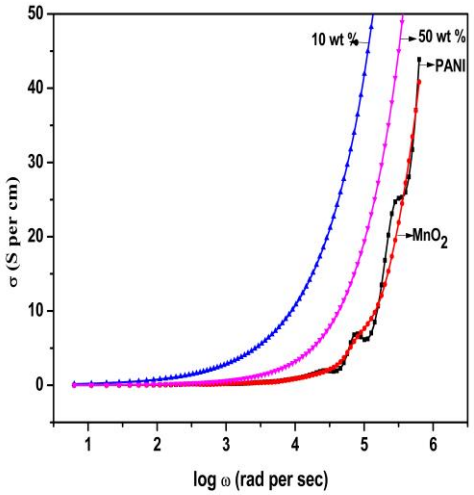

Fig. 4. Conductivity of a) pure PANI, b) pure MnO_2, and c,d) ten and fifty weight percentage of PANI / MnO_2 nanocomposites.

4. CONCULSION

The ten and fifty weight percentage of PANI/MnO_2 nanocomposites has been synthesized. The different type of studies has been analyzed in PANI/MnO_2 nanocomposites. The crystalline structure of PANI/MnO_2 nanocomposites was predicted by powder XRD. The functional group of the PANI/MnO_2 nanocomposites was confirmed by FTIR spectra. The absorption was carried out in PANI/MnO_2 nanocomposites by UV-visible spectra. The conductivity of PANI/MnO_2 nanocomposites was carried by impedance spectroscopy. There are large numbers of applications of PANI/MnO_2 nanocomposites such as electrode materials in many rechargeable batteries, superconductors, biosensors, coatings, nanofibres, nanowires and also in specific biogenic applications.

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