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ORIGINAL ARTICLE

Investigations on structural, optical, and AC conductivity of Polyaniline/Manganese Dioxide nanocomposites

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Abstract

A Polyaniline/Manganese dioxide (PANI/MnO_2) nanocomposite contains five weight percentages of MnO_2. It has been successfully prepared by in situ polymerization. The structural, optical, and conductivity of nanocomposites remain relative to changes with respect to the weight percentage of MnO_2. The structural, morphological, optical, and electrical conductivity investigation of pure MnO_2, pure PANI, and nanocomposites were done with powder XRD, HRTEM, SEM, FT-IR, UV and Impedance spectra. XRD results of the PANI/MnO_2 nanocomposites say that the crystalline structure is converted into a very less crystalline structure due to the incorporation of MnO_2 which is inside PANI chain. The HRTEM and SEM images are confirmed to the nanocomposite formation, morphology studies and also supported to the XRD results. From the optical spectra, MnO_2 nanoparticles have been impressed in the surface of PANI. It works as the compensator in the formation of nanocomposites. UV spectral analysis reveals that the absorption of MnO_2 modifies the absorption wavelength of under visible light in whole range. The absorption wavelength of nanocomposites is 288 nm and 337 nm. AC electrical conductivity of the prepared nanocomposites from impedance spectroscopy was carried out and compared with pure materials. The AC conductivity of as-prepared nanocomposites has been analyzed in the range of 298 K to 423 K. The AC conductivity of nanocomposites varies depending upon a change of logarithmic frequency.

Keywords: *Conductivity; Nanoparticles; Polyaniline; Polymerization; Surface.*

How to cite this article

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INTRODUCTION

As nanocomposites are used in many effective applications, its growth is very high in twenty-first century [1]. Since nanocomposite has unique properties, there was much attraction all over the world towards unique properties in researcher. Nanocomposite is the most promising application field of recent research and technical applications. Combination of the desired properties, materials, and composites increases their high potential applications in futures [2]. The selection of the ingredients of nanocomposites like polymer/metal oxide composite leads to the important application of considerable materials [3]. As physical and chemical properties are good, much interest is shown on nanocomposites material in this research [4]. Some electric conducting polymer has been conjugated in between the chemical bands and monomers, and beneath special doping condition. The conductivity of the polymer electron has taken care [5]. This type of polymer shows that the new materials are manufactured for different applications. The above

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mentioned behaviour are seen in polyaniline (PANI). Metal oxides occupied a principle role in many fields of physics and material science. The metal oxide has easily embraced a structural behaviour with an electronic structure. So, the insulator, semiconductor and metallic behaviour are explained easily [6]. This phenomenon has been found in manganese oxides and chemical applications have long been used as technological importance. However, MnO_2 exhibits an electrochemical capacitance in comparison with another oxidation [7,8]. PANI/MnO_2 nanocomposites were prepared in order to increase the performance of Manganese dioxide [9-11]. Among these polymers, PANI/ Manganese dioxide nanocomposites have many applications because the capacitance of these nanocomposites was increased compared with that of pure MnO_2 due to the high conductivity of PANI and the correlation effect between PANI and MnO_2 [12]. Preparation and studies of PANI/MnO_2 nanocomposites have attracted much attention due to small amount and environment friendliness of the active mange and also due to a good coating layer to restrain MnO_2 from dissolution in acidic environment [11]. PANI can be prepared using many routes [13]. Oxidation methods of aniline are easy to prepare via simple electrochemical or chemical [14]. The wide range applications of PANI are anti corrosion coating, sensors and batteries [15]. It is known from many research articles that the preparation of PANI/Manganese dioxide nanocomposites was used in electrochemical method. However, it's known that no work has been done on prepared nanocomposites for PANI/Manganese dioxide via in situ polymerization method with HCl and Ammonium per sulphate as oxidant. In this paper, the initial work is described and it has been utilized for optical and structural study of PANI/MnO_2 nanocomposite.

MATERIALS AND METHODS

Chemicals

Chemicals, used in this work, are aniline, Ammonium per sulphate, HCl, MgSO4, MnC_2O_4, NaOH and deionized water. These chemicals were purchased from MERCK (analytical reagent grade) and ammonium per sulphate was purchased from RANBAXY (analytical reagent).

Synthesis

Manganese Dioxide Nanoparticles Preparation

Two varied salts ($MnSO_4$ and MnC_2O_4) have varied molarities are added and stirred at 60°C in one hr. While stirring, sodium hydroxide was mixed with solution to reach 12 pH values. The stirring was continued for one hour at 60°C. Then the stirring solution was kept at 30°C in oven and kept out for two hr to become cool. Synthesized brown precipitate was filtered with de-ionized water and cleaned with ethanol. Brown colour precipitates were dried for three days at normal temperature.

PANI nanoparticles preparation

4.5 ml aniline was injected into 70 ml of hydrochloric solution. After 6 hours, preparations of 4.5 gram of ammonium per sulphate were dissolved in twenty ml de-ionized H_2O and it was mixed into prepared solution with constant stirring. The polymerization was developed to proceed for three hours at 60^0C. The reaction solution was filtered, washed with 2M HCl and de-ionized H_2O. Afterwards, it is dried at 90^0 C in vacuum for 1 day to get a green powder.

PANI / MnO_2 nanocomposite (Five Weight Percentage) preparation

Five weight percentages of Polyaniline/ Manganese dioxide nanocomposites was synthesized as follows: 4.5 ml aniline was injected into 70 ml of 2M of HCl which contains MnO_2 nanoparticles of 0.09g (5 weight percentage). After six hrs, 4.5 g of APS was taken and dissolved in 20ml deionized water. Here, the first prepared solution is mixed to drop wise and stirred at 60°C for 30 min. The reaction solution was filtered, washed with two morality HCl and deionized water. Afterwards, it is dried at 100^0C in vacuum for two days to obtain a green powder.

Experimental

The Powder XRD of the prepared samples were characterized using powder X-ray diffractometer (XPERT-PRO using CuKα1, λ=0.1540 nm radiations). The sample was scattered by the angle 2θ values as 10^0 to 80^0. The formation of nanocomposites carried out the High Resolution Transmission Electron Microscope using JOEL JEM 2000 and Scanning Electron Microscope using VEGA3 TESCAN. The powder sample was recorded by FT-IR spectrum using FTIR (JASCO FTIR-4100) in range of wavelength as 399.1927-4000.6047cm^{-1}. The sample was recorded by optical spectrum using UV Visible spectroscopy (UV-2600) in range of wave number as 200-1200 cm^{-1}. The AC conductivity was recorded in the frequency range of 1 Hz to 8 MHz

by impedance spectroscopy (Zahnner zennium IM6 meter).

RESULTS AND DISCUSSION

Structural Analysis

XRD Studies

The Powder X-Ray diffraction studies were used to analyse the structure and crystalline behaviour of the PANI, MnO_2 and PANI/MnO_2 nanocomposites. Fig. 1(a, b, and c) shows powder X-ray diffraction of polyaniline, manganese dioxide particles, and 5 wt % PAIN/MnO_2 nanocomposites. The manganese dioxide nanoparticles indicate that it evinces a broad diffraction peaks occurred between 25° to 60° (Fig. 1(b)) and it was confirmed to crystalline behavior [16]. The MnO_2 peaks of 2θ = 50°, 42°, 39°, 36°, 28°, 25° are the characteristics. The MnO_2 nanoparticles were identified using permanent JCPDS file number 44-0141. MnO_2 has a tetragonal structure which is nice agreement with some research articles [16]. The MnO_2 parameters of unit cell are a=9.784Å, b=9.784Å and c=2.863Å [19]. The MnO_2 nanoparticles boundary size is 26 to 30 nm in some research papers [17, 18]. In these experiments, average crystallite diameter of manganese dioxide is 20 nm and is found by Debye Scherrer's formula (Crystallite size D = 0.9λ/β Cosθ). From the Fig. 1(a), PANI also shows the broad diffraction peaks in the range between of 10° to 45°, it also confirms the behavior of crystalline. The PANI peaks of 2θ = 33°, 28°, 22°, 11° are the characteristics. The PANI nanoparticles were identified using permanent JCPDS file numbers 53-1891. The particle grain size is 8 to 9 nm in few research papers [20]. The powder X-ray diffraction pattern of (5wt%)

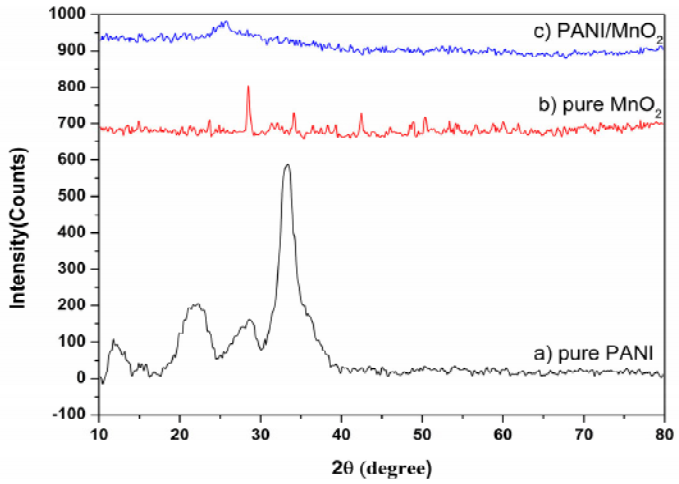

Fig. 1. X-ray diffraction pattern of (a) pure PANI, (b) pure MnO_2 and (c) Five weight percentage of MnO_2/PANI nanocomposite.

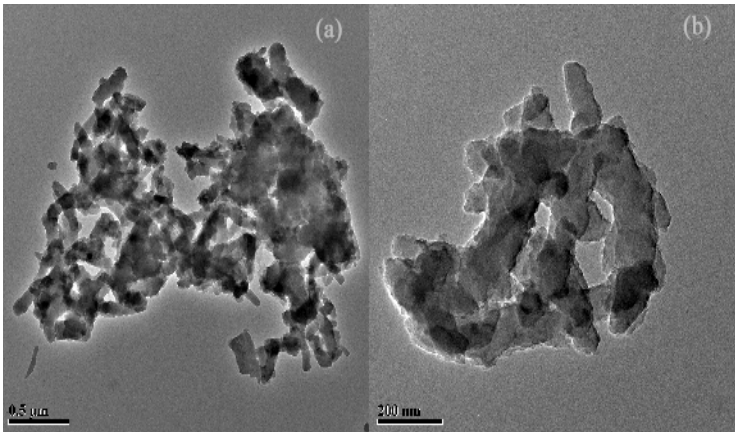

Fig. 2 (a and b). HRTEM image for five weight percentage of PANI/MnO_2 nanocomposites.

PANI/MnO_2 nanocomposites figure is shown in 1(c). In the presence of MnO_2 in PANI, crystalline behaviour of nanocomposites was fully changed. As expected, 5wt% of MnO_2 has affected the PANI chain while they may make changes in the properties of conducting polymer. From the Fig. 1c, nanocomposites do not have any broad peaks in the range between 10° to 80°, and it confirms the interaction of MnO_2 and PANI by the formation of nanocomposites. These results show that the 5 wt% of PANI/MnO_2 nanocomposites is decreasing the crystallite nature. The nanocomposites structural behaviour has been confirmed by HRTEM and SEM analysis.

High Resolution Transmission Electron Microscope (HRTEM)

Fig. 2 (a and b) shows the HRTEM images of PANI/MnO_2 nanocomposite. The inset MnO_2 nanoparticles show figures in black. The MnO_2 nanoparticles were embedded in the PANI matrix forming core shell structure; it is shown in Fig. 2. The HRTEM image indicates that the nanocomposites particles have uniform dispersion with irregular shaped morphology. The grain boundaries in the strip could not be found correctly. However it is found that the edges of very small particles connect to large particles. So it should be noted that the size of the MnO_2 islands is not uniform. It confirms and supports the XRD analysis.

Scanning Electron Microscope (SEM)

Morphologies of the PANI/MnO_2 nanocomposites were examined using SEM techniques. Fig. 3 (a and b) represents the SEM micrographs of the PANI/MnO_2 nanocomposites. Manganese dioxide is intercalated between polyaniline layers and is maintained. The SEM image of PANI/MnO_2 nanocomposite is composed of more than two nanoparticles which are connected to each other

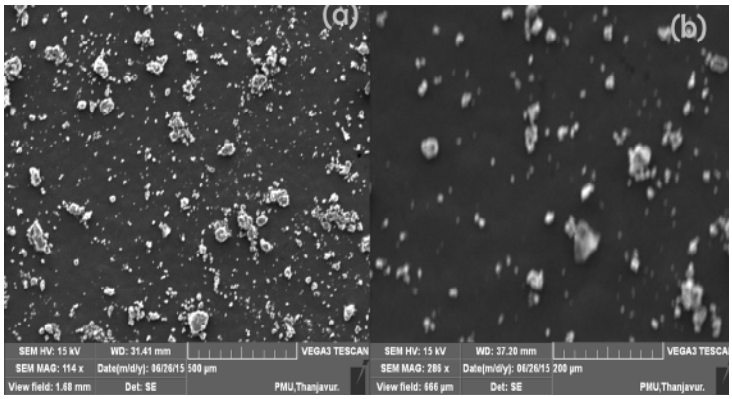

Fig. 3 (a and b).SEM images for five weight percentage of PANI/MnO_2 nanocomposites.

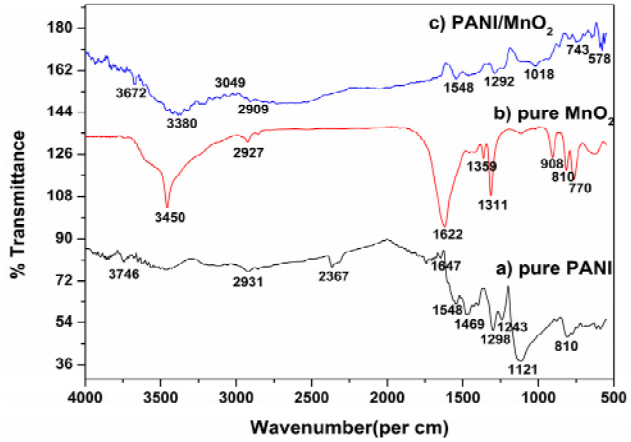

Fig. 4. FTIR spectra of (a) pure PANI, (b) pure MnO_2 and (c) Five weight percentage of PANI/ MnO_2 nanocomposite.

resulting in a porous structure. It also confirms the results of XRD analysis.

Optical Analysis

FTIR Spectroscopy

Structural information and functional group was identified using FTIR spectroscopy of five weight percentage in PANI/MnO_2 nanocomposite. Fig. 4(a) shows that the peaks at 2931, 2367, 1647, 1548, 1469, 1298, 1121 and 810 cm^{-1} are pure PANI. Fig. 4(b) shows that the peaks at 3450, 2927, 1622, 1311, 908, 810 and 770 cm^{-1} are pure manganese dioxide nanoparticles. Fig. 4(c) shows that the peaks at 3672, 1548, 1292, 1018 and 578 cm^{-1} are five weight percentages of PANI/MnO_2 nanocomposites. In between the wavenumber of 499 cm^{-1} to 899 cm^{-1}, some absorption bands are placed. Manganese dioxide is the characteristic band of Mn-O bending vibration of octahedral [21]. The manganese dioxide nanoparticles show that wide peak at 3450 cm^{-1} and were associated to the adsorbed H_2O molecule. The peaks 1,292 cm^{-1} is C-N stretching and 1,292 cm^{-1} is C-H bending of PANI [22]. The conductivity of PANI at 1121 cm^{-1} is a very strong peak and the degree of delocalization of electrons was measured. The very weak and small peak 810 cm^{-1} is very near to C-H out of plane bonding in benzenoid ring of PANI chain. Fig. 4(c) clearly shows that the 5 wt % of PANI/MnO_2 nanocomposites was compared to pure PANI and pure MnO_2. The weak peak at 3049 cm^{-1} is shows that the N–H stretching region of nanocomposites (curves c). Comparatively, this peak was very weak in the PANI (curve a). The small peak 578 cm^{-1} indicates the PANI of C-N-C bonding mode of aromatic ring. In nanocomposites peak, 743 cm^{-1} is C-C and C-H bonding in benzenoid ring, 1292 cm^{-1} is C-N stretching of benzenoid ring, 3380 cm^{-1} is vibration band of –OH. All these are indicating as a PANI chain. All the other peaks 3672, 1548 and 1018 cm^{-1} are shifted, and to near of MnO_2 peaks. Formation of nanocomposites and functional group of nanocomposites have confirmed from the figures.

UV - Visible Spectroscopy

Fig. 5(a, b and c) shows UV analysing of pure PANI, Pure MnO_2 and five weight percentage PANI/MnO_2 nanocomposites synthesized as a function of wavelength. The normal temperature UV spectra of Polyaniline/Mamganese dioxide nanocomposites samples were recorded absorption (Fig. 5(c)). The peak at 251 nm (Fig. 5(a)) represents the π–π* electron orbital transition along the backbone of the PANI Chain. As PANI/MnO_2 (five weight percentages, Fig. 5(c)) is combined with PANI and MnO_2, the peak assigned to the polaron–π* transition of the PANI chains shifted to a higher wavelength area. It indicates the interaction between quinoid rings and nanocomposites as written in some article. Regarding the first change was started at 288 nm, the π–π* electron transition of quinoid ring requires small energy for absorption with the presence of PANI/MnO_2 nanocomposites [23]. The maxima red shifted up to 337 nm for five weight percentage of PANI/

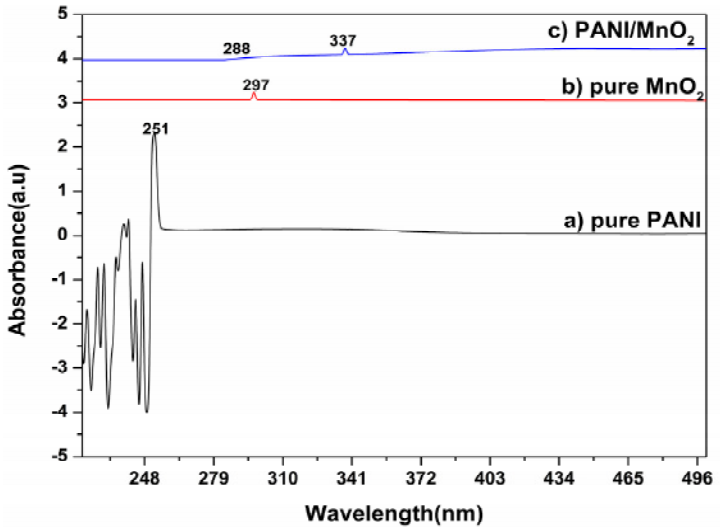

Fig. 5. UV-Visible spectra of (a) pure PANI, (b) pure MnO_2 and (c) Five weight percentage of PANI/ MnO_2 nanocomposite.

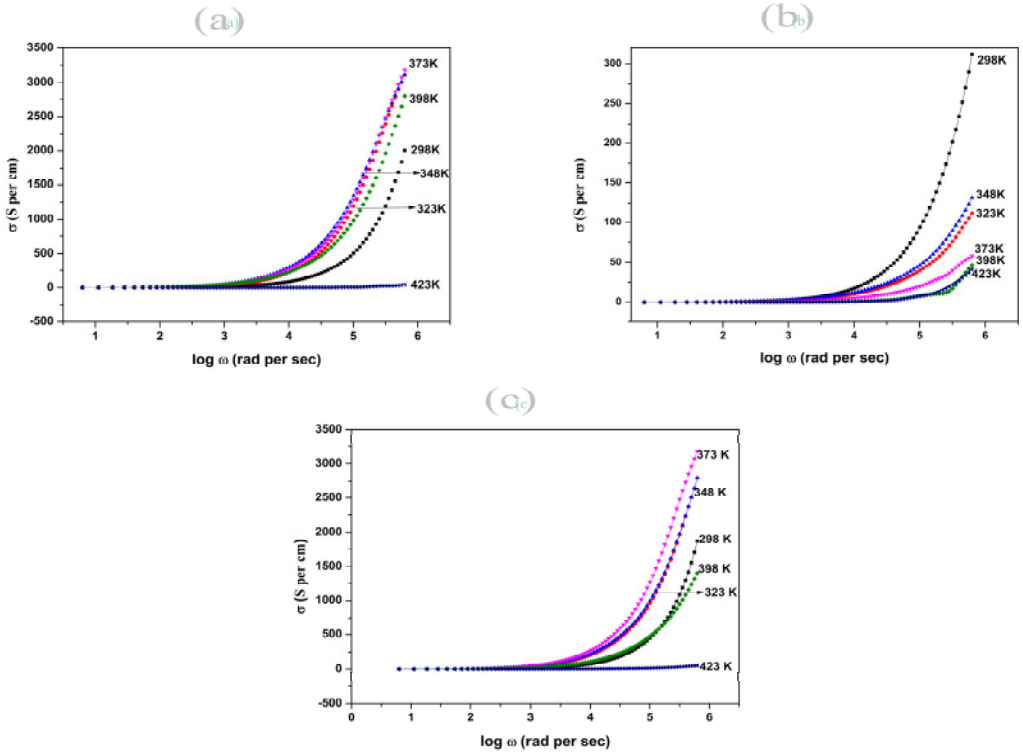

Fig. 6. AC conductivity of (a) pure PANI, (b) pure MnO_2 and (c) Five weight percentage of PANI/ MnO_2 nanocomposite.

MnO_2 compared to 251 nm and 297 nm of neat PANI and MnO_2 nanoparticles.

Conductivities Analysis

The AC electrical conductive (σ_{AC}) as a function of frequency at different temperatures are shown in Figs. 6(a, b and c) of pure PANI, MnO_2 and PAIN/MnO_2 nanocomposites. The conductivity curve of pure nanoparticle and nanocomposites can be classified into three parts: Part I: For pure and composite nanomaterials at all temperature, conductivity is constant in between the frequency ranges of 0.5 to 2.5 rad per sec. The charge carrier motion is rest in these materials for because of constant conductivity. Part II: All materials at all temperature, conductivity slightly increase in between the frequency ranges of 3 to 4.5 rad per sec. The charge carrier motion is lightly flow in these materials because of the increasing conductivity. Part III: For pure PANI (Fig. 6(a)), conductivity is minimum at high temperature and maximum at average temperature. For pure MnO_2 (Fig. 6(b)), conductivity is maximum at very low temperature, but composite materials, conductivity is totally varied compared to the pure materials. The conductivity of the PANI/MnO_2 nanocomposites materials is maximum at normal temperature (Fig. 6(c)). The composite materials conductivity is high to compare with the pure materials.

CONCLUSION

In present work, pure and nanocomposites materials were successfully prepared via In Situ Polymerization technique and they were carried out by various studies. Powder X-ray diffraction spectrum predicted the crystalline results in this work. It confirms the nanocomposites with PANI and MnO_2 nanoparticles. The formation and functional group of the nanocomposites was identified from fourier transform infrared spectra. UV-visible absorption of the all prepared samples, shown, show the absorption peaks at visible region due to MnO_2 in the polyaniline chain. The impedance spectroscopy studies were successfully carried out and conductivity was discussed between the frequency ranges of 1 Hz to 5 MHz. There are many potential applications of Polyaniline/Manganese dioxide nanocomposites such as in the field of electrode

in different rechargeable batteries, nanoscience and bioscience applications.

CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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