

Structural Characterization of PANI\MnO₂ polymer Nanocomposites

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Abstract: - Polyaniline \ manganese dioxide (PANI/MnO₂) nanocomposites have been synthesized MnO₂ nanoparticles into the PANI matrix by in situ polymerization method. The composite formation and structural changes in PANI/MnO₂ nano composites were investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR).XRD pattern of PANI/MnO₂ nanocomposites exhibited sharp and well-defined peaks of tetragonal phase of MnO₂ in PANI matrix. SEM images of the composites showed that MnO₂ nanoparticles were dispersed in the PANI matrix. The FT-IR analysis revealed that there was strong interaction between PANI and MnO₂.

Keywords: MnO₂, Polymer nanocomposite, in situ polymerization, XRD, SEM.

I. INTRODUCTION

Transition metal oxide plays on key role for many potential applications but its conductivity has been low. Polyaniline becomes on unique and promising conducting polymer with a great potential application in many areas. When combining these two materials a composite has been synthesized. MnO₂ nanoparticles has been synthesized using microwave assisted solution method and PANI\MnO₂ nanocomposites has been synthesized using in situ polymerization method. To improve the properties of both PANI and MnO₂ composite material has been prepared.

Manganese dioxide has been widely used as a electrode material for electrochemical capacitance due to low cost and wide abundance and environmental friendliness. The theoretical capacitance of MnO₂ has been very high but the poor electrical conductivity limits its actual specific capacitance .In order to improve the conductivity of manganese dioxide, polyaniline has been interacted with it. Polymer nanocomposites materials have been hybrid properties.

Various methods are used to synthesize MnO₂ nanoparticle including hydrothermal reaction [1], thermal decomposition [2], electrodeposition [3,4], template method [5] and micro emulsion method [6,7]. Among them microwave assisted solution method. It has the advantage of homogeneous volumetric heating, high reaction rate and energy savings as compared with conventional heating method [8,9]. The nanocomposites obtained through the interaction of PANI and MnO₂

shows enhanced hybrid properties due to synergistic effect [10].

Polyaniline is one of the most promising conducting polymers due to its ease of preparation and good environmental stability. PANI has been synthesized many methods by chemical electrochemical oxidation methods of aniline. PANI has a wide range of applications such as anticorrosion coating, batteries and sensor [11,12]. In this paper PANI\MnO₂ polymer nano composite has been synthesized in situ polymerization method. The structural and optical characteristics of PANI\MnO₂ were studied.

II. MATERIALS AND METHODS

2.1 Materials

The AR grade aniline (Merck) was purchased and distilled prior to use. Ammonium per sulphate analytical reagent (RANBAXY), Hydrochloric acid , Manganese II sulphate, Manganese oxalate and sodium hydroxide are also used(AR grade Merck).

2.2 preparation of MnO₂ nanoparticle

Manganese oxalate and manganese sulphate of two different anions of manganese salts are used to synthesize MnO₂ nanoparticles. Both salts are taken 0.25 M mixed with stirring at room temperature. During stirring NaOH solution were added drop by drop till the PH value of the solution becomes 12. Stirring was continued for 1 hour till the solution becomes of uniform mixing. The solution turns into brown in colour and then this solution transferred into microwave oven kept at minimum temperature. After cooling the particles are filtered and

washed with double distilled water and ethanol dried at 70°C for 5h under air atmosphere.

2.3 Preparation of PANI/MnO₂ nanocomposite

PANI/MnO₂ nano composite samples can be prepared using in situ oxidative polymerization method. HCl and 4.5 ml of aniline can stirred. During stirring 4.5 gm APS dissolved in 20 ml of deionized water and MnO₂ nanoparticles was added drop by drop. The string solution colour changing into deep green which indicates good degree of polymerization. String was continued for further 1 hour. Then the precipitate was filtered and dried. Similarly various wt% MnO₂ nanoparticle has been interacted with polymerization the desired polymer nano composite samples can be formed.

2.4 Characterizations

XRD patterns of the samples were investigated using X ray diffractometer (X PERT PRO P ANALYTICAL, Netherland) to study the crystalline nature. Cu K α radiation of wavelength $\lambda = 1.5406 \text{ \AA}$ was used as a diffraction source and with the step size of 0.05° from the diffraction range 10 - 80°. The morphology studies of samples were studied by Scanning electron microscope (SEM) (HITACI SEM S 2400 device) with an operating voltage 20 kV with the magnification range 7500- 30,000. The structural and morphological studies of the samples were studied by High Resolution Transmission electron microscope (model JOEL – J2000) with the operating voltage at 200 kV. The FTIR spectra of the prepared samples were recorded in the range 400-4000 cm⁻¹ using a Shimadzu 8400S FTIR spectrometer. The materials are finely dispersed in KBr using an agate mortar and then pressed into circular disc of 10 mm diameter and 0.5 mm thickness at a pressure of 250 MPa. These pellets are dried with IR light source. AC conductivity and electrochemical properties of the samples were measured using Hioki (Japan) Model 3532-50 programmable LCR meter. By making 1cm diameter pellets under a hydraulic pressure 10 Kpsi. The contacts are made over the surface of the pellets with the help of conducting silver paste.

XRD

The XRD pattern for MnO₂ and PANI/MnO₂ (1 and 10 wt%) samples were shown in fig 1. From the fig the observed peaks along 36.2°, 32.2°, 59.9° which can be indexed h k l values at (4 0 0) (1 0 0) (2 6 0) well matched with nanocrystalline MnO₂. The broadness of the peaks indicates that the formed compound are mainly nano phased. Good crystalline structure has been evidenced by strong diffraction peaks but in polymer nanocomposite samples the peaks can be shifted from their respective standard positions which may due to PANI matrix. In addition, reduced intensity of the peaks and relatively larger peak broadening compared with

XRD of pure MnO₂. The intensity of the peaks decreases slightly, which is due to interaction between PANI and MnO₂. The PANI attached to MnO₂ Still keep good crystallization contributing to the electrical conductivity.

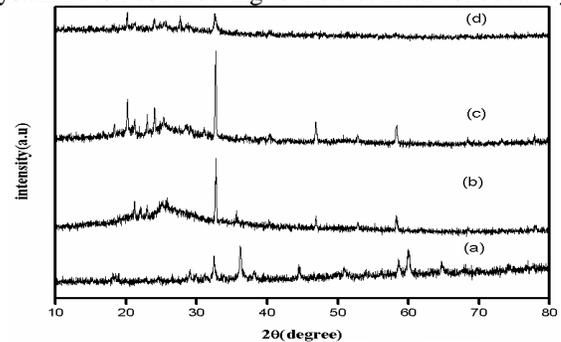


Fig 1: XRD pattern of (a)MnO₂ (b) PANI (c) PANI/1wt% MnO₂ (d) PANI/10 wt% MnO₂

FTIR

The FTIR spectrum was further performed the formation of MnO₂ and organic residue on the surface of MnO₂ nanoparticles. Fig2 shows the FTIR spectra of MnO₂, PANI and PANI/MnO₂(1wt% and 10wt%) nanocomposites. The characteristic IR peaks of Mn- O (507 cm⁻¹), which can be observed in PANI/MnO₂ composites. The peaks at wavenumbers 1400,1496,1562,1301,1147 and 879,815 cm⁻¹ corresponds to PANI. The peaks at Wavenumbers 1490 cm⁻¹ and 1560 cm⁻¹ are attributed to C-N and C-C stretching mode for the quinoid and benzenoid rings. The weak band at around 3000 cm⁻¹ is attributed to N-H stretching. The result of FTIR. Spectrum confirms the presence of both components in the composite. The characteristic absorption band of PANI MnO₂ composites emerge in both MnO₂ and PANI demonstrating the existence of both components in composites.

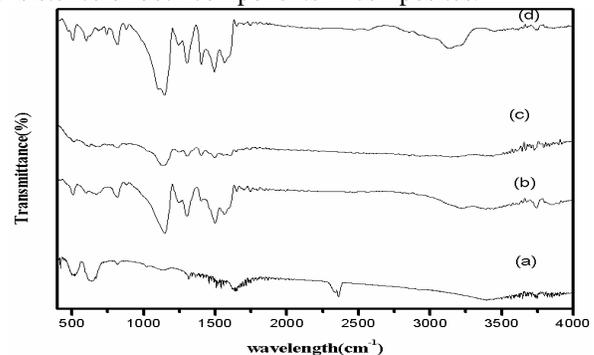


Fig 2: FTIR spectrum of (a)MnO₂ (b) PANI (c) PANI/1wt% MnO₂ (d) PANI/10 wt% MnO₂

Table 2: Functional group analysis using FT-IR for PANI\MnO₂ polymer nanocomposite

Wavenumber(cm ⁻¹)	Assignments
3421	N-H stretching mode vibration
2800	O-H stretching mode vibration
2880	N-H in <u>benzenoid</u> ring
1745	C-CH ₂ stretching vibration
1649	Adsorption of water moisture
1562	C-N stretching mode in <u>quinoid</u> ring
1494	C-C stretching mode vibration for <u>quinoid</u> ring
1400	C-N stretching mode vibration in <u>benzenoid</u> ring
1301	N-H bending in aromatic amine
1315	Bending vibration of O-H bonds connected with <u>Mn</u> atoms
1244	N-H bending and C-H stretching in <u>benzenoid</u> ring
1147	Vibrational modes of N=Q=N (Q refers to the <u>Quinonic</u> type rings)
879	An aromatic C-H out of plane bending vibration
616	<u>Mn</u> -O stretching mode of tetrahedral sites
500	Distortion vibration of <u>Mn</u> -O in an octahedral sites

SEM

Fig 3 shows the SEM micrographs of MnO₂, PANI and PANI\MnO₂ nanocomposite samples. From the Fig it can be seen from these figures that the composite particles are highly dispersed with agglomeration in both the cases and the formation of polymer shell around the nanocrystalline particles can be seen in SEM images, assisting the growth and further aggregates formation indicating diffusion limited cluster aggregation. MnO₂ may be well wrapped inside the PANI According to these results.

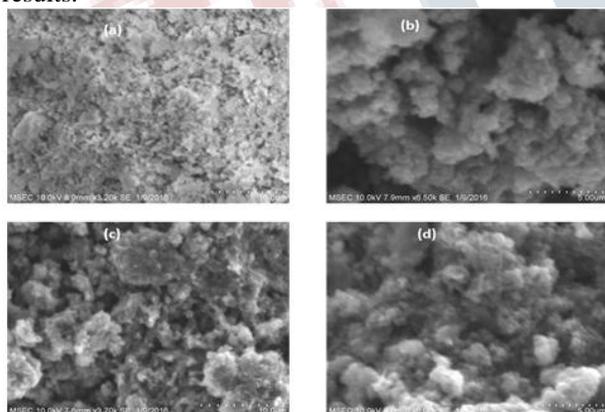


Fig 3: SEM image of (a) MnO₂ (b) PANI (c) PANI/1wt% MnO₂ (d) PANI/10 wt% MnO₂

III. CONCLUSION

In this work in situ polymerization of aniline in the presence of MnO₂ has been studied. PANI\MnO₂ nanocomposite shows great enhancement of morphology than the pure PANI, which indicates that PANI and MnO₂ has been interacted. We expect that this method can be used to produce other polymer metal oxide nanocomposite.

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