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Structural and Optical Properties of Polyindole-Manganese Oxide Nanocomposite

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ABSTRACT

Manganese oxide/poly indole (Mn_2O_3/PIND) hybrid structures have been investigated for their optical properties. Mn_2O_3 nanoparticles prepared by the sol-gel method and characterized by XRD, scanning electron microscope (SEM) and, infrared (IR). The hybrid Mn_2O_3/PIND structure was obtained by the addition of PIND on the surface of Mn_2O_3. The optical properties of the nanocomposite were determined from UV and PL studies. The energy band gap of the materials was obtained from the absorption wavelengths of the UV-visible spectrum.

***Key words**: Manganese Oxide; Optical Property; Poly indole; Nanocomposite.*

1. INTRODUCTION

In the large field of nanotechnology, conducting polymer matrix based nano composites have become a prominent area of current research and development. Their electrical and electrochemical properties show great promise for commercial applications in rechargeable batteries, Schottky diodes, light emitting diodes, transistors etc [1-3]. Composite materials of conducting polymers and electro active metal oxides are of great interest in electronic applications [4-5]. Polymers reinforced with nano metal oxides become popular every day because of their improved mechanical strength, flexibility in designing besides better chemical, electrical and optical properties [6]. In the last years, the polymer doped with metal oxide nanoparticles have been studied as alternative materials for optical applications, including planar waveguide devices and micro optical elements [7-10]. The polymers modified by metal oxide nanoparticles have been prepared by sol-gel process, by polymerization of monomer containing nanoparticles and by dispersing of nanoparticles in a polymeric matrix [10-14].The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the material and it is possible to control these properties, including the refractive index, by concentration and size of the particles.

In the present study polyindole based manganese oxide nano composite was prepared and analyzed.

2 . EXPERIMENTAL

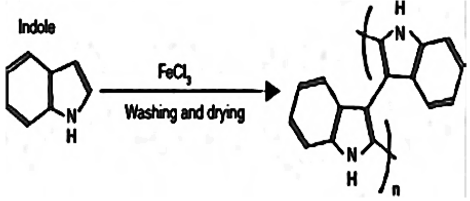
2.1. Materials and Preparation of the Nano Metal Oxides

Synthesis of Manganese Oxide Nano Particles:

Mn_2O_3 nanoparticles were synthesized by sol-gel method. Manganese sulphate ($MnSO_4.H_2O$) as precursor and water as the solvent were used for the preparation. To the vigorously stirred solution of $MnSO_4$ H_2O (0.1M),a 0.1 M solution of NaOH was added drop wise using citric acid as the caping agent. The manganese hydroxide precipitate formed was washed several times in distilled water to free it from ions and other impurities. The wet precipitate obtained was dried at room temperature and thoroughly grounded using an agate motor to obtain the manganese hydroxide precursor in the form of fine powder. The powder so obtained was annealed at 500 °C for 3 hours in a muffle furnace to obtain nano powder of manganese oxide.

Synthesis of Polyindole and Mn_2O_3/Polyindole Interfaces:

At first polyindole was synthesized by chemical oxidation of indole using $FeCl_3$ as oxidant in water medium (Scheme 1). 100 ml of water is taken in a conical flask to which 0.1 M of indole was added and stirrered well. To this 0.1 M $FeCl_3$ solution was added and stirred for 24 hrs. The colour of the reaction mixture changed from colourless to dark brown due to polymerization. The residue was dried at room temperature to obtain polyindole.



Scheme 1: Preparatoion of Polyindole.

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Mn_2O_3/PIND hybrid interfaces were prepared by adding desired amount of Mn_2O_3 in the PIND dispersion followed by stirring well for 2hrs.

2.2 Characterizations

X-ray diffractogram (2θ=10-90°) was obtained on XPERT-PRO powder diffractometer with Cu-Kα radiation. The FTIR spectrum was recorded using KBr wafer on the Thermo Nicolet FTIR model AVATAR 370 DTGS. The surface morphology of the powdered samples were obtained by scanning electron microscope JEOL/EO JSM-6390 .The absorption spectra were recorded at room temperature using SHIMADZU UV-2550 UV Visible spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis:

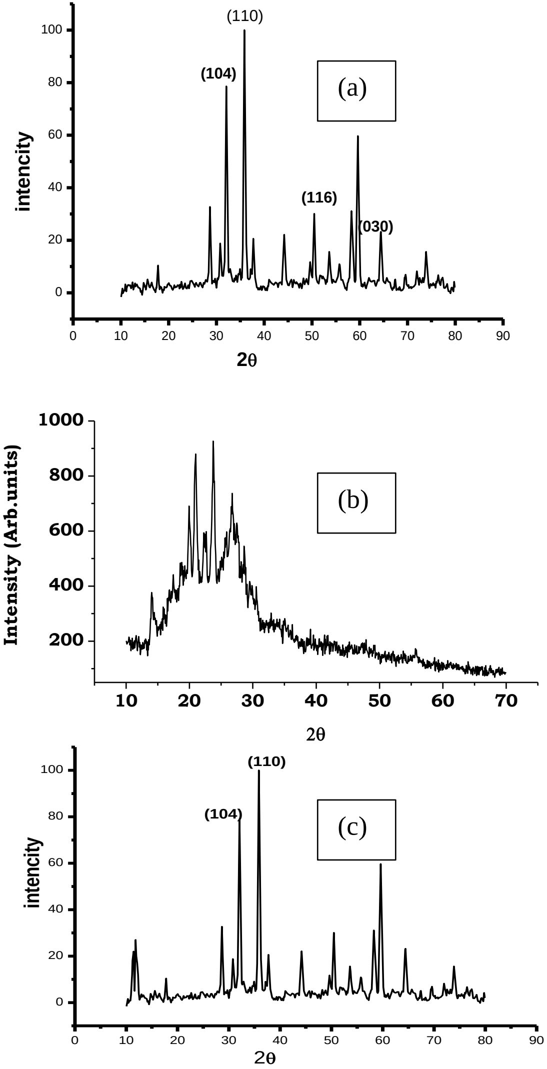

Figure 1: XRD spectrums of a) Mn_2O_3 b) poly-indole, and c) Mn_2O_3/polyindole.

Figure 1 shows the XRD patterns of Mn_2O_3, poly indole and Mn_2O_3/poly indole hybrid interface. The average crystallite size of the powders were determined by using Scherrer's formula, D = 0.9λ/βCosθ, where D is the average crystallite size in nm, λ the wavelength of X-ray radiation, θ the Bragg's angle and β the full width at half maximum of the peak observed for the samples [15].

Figure 1 (a) clearly reveals Rhombohedral nature of Mn_2O_3 nanoparticles. The peaks were found to be matching with standard JCPDS value of Mn_2O_3. The average particle size of samples is in the range 26 nm. Figure 1(b) is the XRD pattern of polyindole showing a broad hump which suggests an amorphous structure which is the characteristic of polyindole. Figure 1(c) is the XRD pattern of Mn_2O_3/PIND interface which shows all the characteristic peaks of Mn_2O_3.

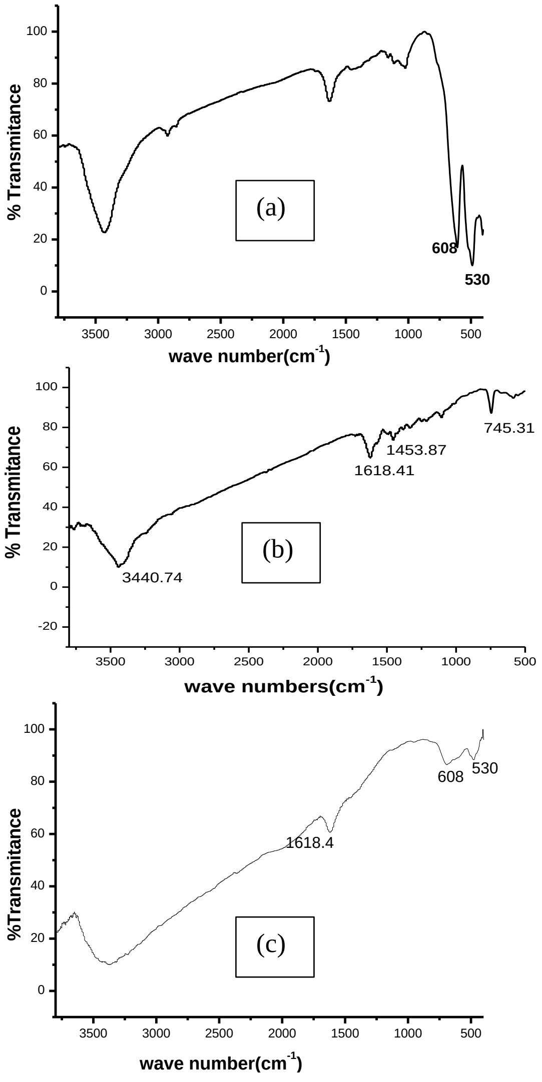

Figure 2: FTIR spetrums of a) Mn_2O_3, b)polyindole and c) Mn_2O_3/polyindole

A close examination of the FTIR spectra shows that Mn_2O_3 shows strong peaks at 530 and 608 cm^{-1} (fig.2a) .In the case of polyindole (Fig.2b) the sharp band expected at about 3200 cm^{-1} for the bonded N-H stretch is absent, indicating the participation of nitrogen in polymerization. Peaks at 1458 cm^{-1} are induced by aromatic alkene, 1331 cm^{-1} is due to C-N vibration and 744 cm^{-1} is due to the bending mode of aromatic alkene. The weak band at 1105 cm^{-1} corresponds to oxidized form of polyindole. It is inferred that the chloride ions from the oxidant serve as counter ions for oxidized polyindole. The IR spectrum of Polyindole based manganese oxide nanocomposite shows all the characteristic vibrations of polyindole and Mn_2O_3.

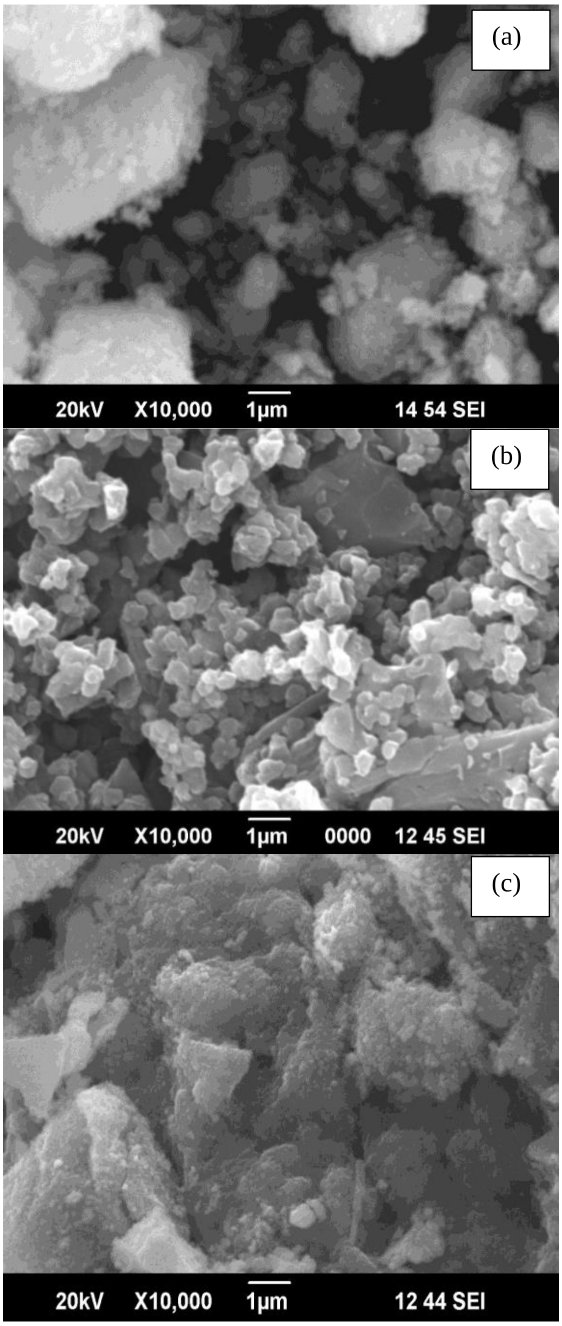

Figure 3: SEM images of a)Mn_2O3, b)polyindole and c) Mn_2O_3/polyindole.

3.2 Morphological studies:

SEM images of Mn_2O_3 shows aggregates of solids of different sizes (Fig. 3a). whereas Polyindole shows a spherical pattern (Fig.3b). But the SEM image of the composite (Fig.3c) is different from both the polymer and metal oxide.

The nature of interface so formed between Mn_2O_3 and PIND can be visualized as adsorption of organic entities on the oxide base, giving rise to a change in morphology of the host matrix. This dynamic transition in morphology is the manifestation of the physico-chemical interactions which occurs due to variation in interfacial energy between the inorganic nanoparticles and the organic dispersion. However, the exact mechanism of growth and corresponding kinetics of the formation of such structures is not clear [15].

3.3. Optical Analysis:

UV-Visible spectroscopy was employed to understand the optical behavior of rhombohedral Mn_2O_3 nanoparticle, Mn_2O_3/polyindole interface and PIND dispersion. Optical absorption spectra for all the three are shown in figure 4. UV spectrumgives information about excitonic or inter band transition of nano materials. The fundamental absorption which corresponds to electron excitation from the valence band to the conduction band is used to determine the nature and value of the optical band gap. The relation between absorption coefficient, α, and the incident photon energy, hν, is given by the relation, $\alpha h\nu = A\ (h\nu\text{-}Eg)n$, where Eg is the band gap of the material, A is the absorption coefficient and the exponent n depends on the type of transition. The value of band gap is determined by plotting $(\alpha h\nu)1/n$ versus hν and extrapolating the straight line portion to hν axis(fig.5). When the energy of the incident photon is less than the band gap, the increase in absorption coefficient is followed with an exponential decay of density of states of the localized band into the gap. The absorption edge here is called Urbach edge, α. Urbach energy characterizes the extend of the exponential tail of the absorption edge. The width of the Urbach tail is an indicator of defect levels in the forbidden gap. The following relation is used to calculate the Urbach tail, Eu., $\alpha(\nu) = \beta \exp(h\nu/Eu)$

where β is a constant, Eu is the Urbach energy which indicates the width of the band tails of the localized states, h is the Plank’s constant and ν the frequency of incident photons. The natural logarithm of the absorption coefficient, α(ν), was plotted as a function of the photon energy, hν(Fig.6). The value of Eu was calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of curves. The exponential absorption tails, i.e. Urbach energy, depends on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds and on average photon energies [16].

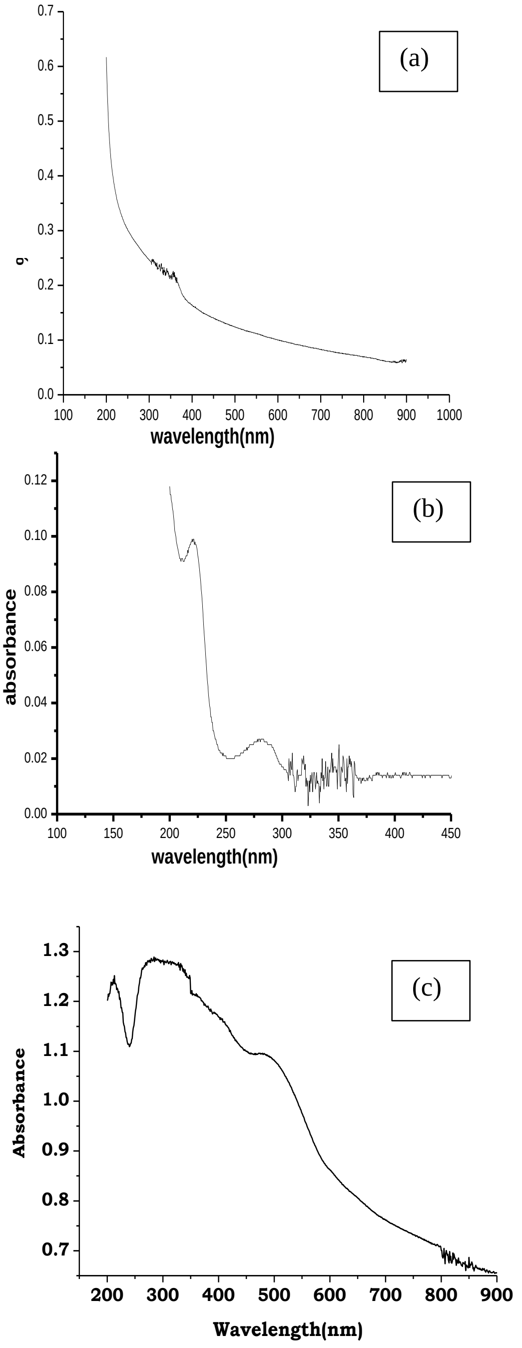

Figure 4: UV Visible spectrums of a) Mn_2O_3, b) polyindole and c) Mn_2O_3/polyindole

A clear band edge at 363 nm in figure 4(a) is the characteristic of Mn-O vibration. Figure 4 (b) shows a band edge of 503 nm and peaks at 445 nm and ~670 nm corresponding to PIND. Figure 4(c) corresponding to the nano composite of Mn_2O_3/ PIND, shows a peak at 330 nm which is due to the π-π* transitions. The bands at ~420 and ~850nm refer to n-π* and n-π transitions respectively and signifies the formation of polarons which depends on amount of metal oxide The band gap and other optical parameters are given in the table 1. The band gap has an inverse dependence on the grain size

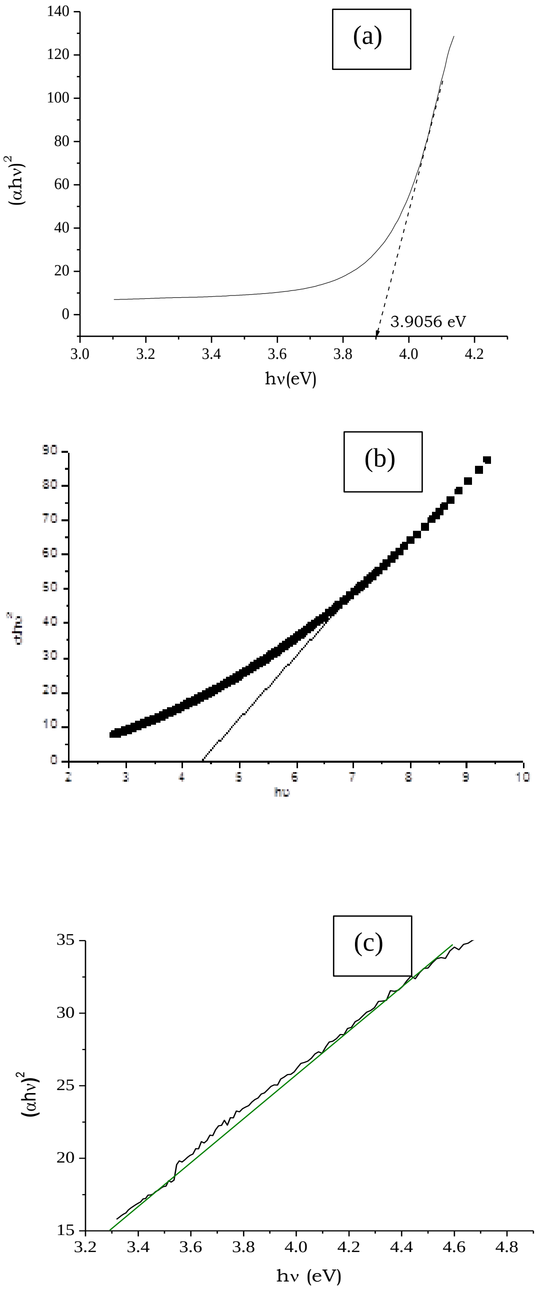

Figure 5: $(\alpha h\nu)^2$ versus photon energy in eV of prepared samples of a) Mn_2O_3 b)polyindole c) Mn_2O_3/polyindole .

Table 1: Optical parameters and the particle size for prepared samples

Samples	**Part-icle**	**λ_{max}**	**Eg (Tauc)**	**Eg λ_{max}**	**Eu**
Mn_2O_3	26	363	3.42	3.09	1.41
PI	246	445	2.79	4.4	2.18
Mn_2O_3/ PI	ND	420	3.10	3.3	1.91

4. CONCLUSIONS

XRD spectrum confirms that the as prepared Mn_2O_3 is crystalline form. This result is in good agreement with the particle size calculated using

Scherrer equation from the XRD data.XRD spectra reveals the formation of composite material. From the FTIR spectrum, the major stretching and bending vibrations are identified and it clearly indicates the presence of polymer metal oxide composite formation. Optical absorption in the UV-Vis region indicates that polyindole has direct band gap which decreases with hybrid formation from 4.4eVto 3.3eV.

Acknowledgements

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Biblographic Sketch

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