

Structural and Optical Properties of ZnO and ZnO/PS Core-Shell Nano Composites

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Abstract

The Core-shell structured nanoparticles of ZnO-PS were successfully synthesized in PS matrix by wet chemical method and transparent thin films of these nano-hybrids were coated on substrates by using spin coating technique. The XRD spectra of ZnO nanoparticles demonstrates a series of characteristic peaks that were in accordance with the XRD pattern of wurtzite phase, hexagonal ZnO structure. The crystallite sizes in ZnO, and ZnO/PS, corresponding to 101 plane, are found. Structural and optical properties of all the nanocomposites samples were investigated by XRD, HRTEM, EDX, FTIR and UV-Visible spectroscopy.

Keywords : Polystyrene, ZnO, structural and optical parameters

1. Introduction

Nano-particles are frequently delineated as engineering groups of less than 100 nm size with different shapes. The Nanoparticles have generally improved chemical, as well as, physical properties in comparison to the bulk polycrystalline materials or single crystals because of the large surface area per unit mass and possess high reactivity as a consequence of quantum dimensions[1,2]. Nanoparticles are rapidly gaining importance in various sectors, such as food and feed, health care, environmental health, mechanics, optics, specialties in the medical sciences, physics, chemical industries, drug and gene administration, industrial area, energy science, catalysis, optoelectronics, optical devices and photo electrochemical requisitions. Polystyrene (PS) is a universally useful, surely understood, every now and again used, light weight, renowned plastic with commendable dimensional accuracy, easy synthetic processing, simple handling and less cost[3, 4]. It has been generally used in gadgets, family unit machines, packing materials, and so on. Some of the very important metal oxide inorganic particles include Magnesium oxide (MgO), Zinc Oxide (ZnO) and Titania (TiO₂). Due to broad band gap, MgO

has been used in many applications, for instance catalysts, removal of toxic waste, dense combustible oils, as adsorbents, refractories, ferroelectrics, anti-reflective and reflective coatings. A study by Tang and Lv [24] on the production of the antibacterial system and the antibacterial movement of the metal oxide nanoparticles, showed that magnesium oxide (MgO), Zinc Oxide (ZnO) and Titania (TiO₂) could be used as a part of the commercial products, such as surface cleaners, sportswear, computer gadgets, solar powered panels and disinfectants for uncontaminated stench[5].

Polystyrene has been selected as a host matrix in this study due to its superlative properties i.e. amorphous nature, optically transparent, thermoplastic nature and very high flexibility as thin films. At room temperature polystyrene is in a solid state, flows when heated above the glass transition temperature and solidifies again when cooled. The introduction of the metal oxide fillers into the matrices of polymers can generally alter the properties of polymers i.e. optical, electrical and mechanical [6-8]. The nano composite made by reinforcing metal oxide nanoparticles to polystyrene have highly promising optical properties.

There had been unprecedented advancements in the field of nanomaterials in general and Core-shell nanoparticles and nanocomposites in particular [9-14]. The main aim of research is to achieve advanced multi functionality properties and to develop and standardize new approaches of manufacturing the nano-hybrid materials of two dissimilar phases like coating the inorganic nanoparticles with polymeric phase or developing the nanoparticle reinforced polymeric matrices with tunable characteristics as per the need of the application.

The research work reported in the literature mainly concentrate on the preparation of Core-Shell nanocomposites by different techniques; Sol-gel Method, Physical Vapor Deposition, Chemical Vapor Deposition, Co-precipitation Method, Hydrothermal Method, Pulsed Laser Method and Solution Combustion or Auto Ignition Method. The wet chemical methods had always played a very important role in developing newer materials. Core-Shell nanocomposites prepared by chemical methods showed promising characteristics. The chemical methods are always superior over others routes simply because of their operational simplicity and intimate direct reaction among reactants, which minimizes the chances of contamination.

Thus for synthesis of high quality of materials with improved properties. Wet Chemical methods is best suited process. Therefore, in the present work, main focus is on the synthesis and characterization of Metal oxide core-shell structures by chemical methods, where Metal can be Magnesium and the shell can Polystyrene, The structural and optical properties of metal oxide core-shell structures were investigated and distinctive features were studied in detail. In the present course of research work we have synthesized the core-shell nanostructure PS-ZnO and coat the thin film on the glass substrate by using spin coater. Similarly, the core-shell structured nanoparticles of ZnO with PS were prepared by performing direct in situ polymerization of styrene monomer by mixing the ZnO nanoparticles simultaneously.

2. Experimental Part

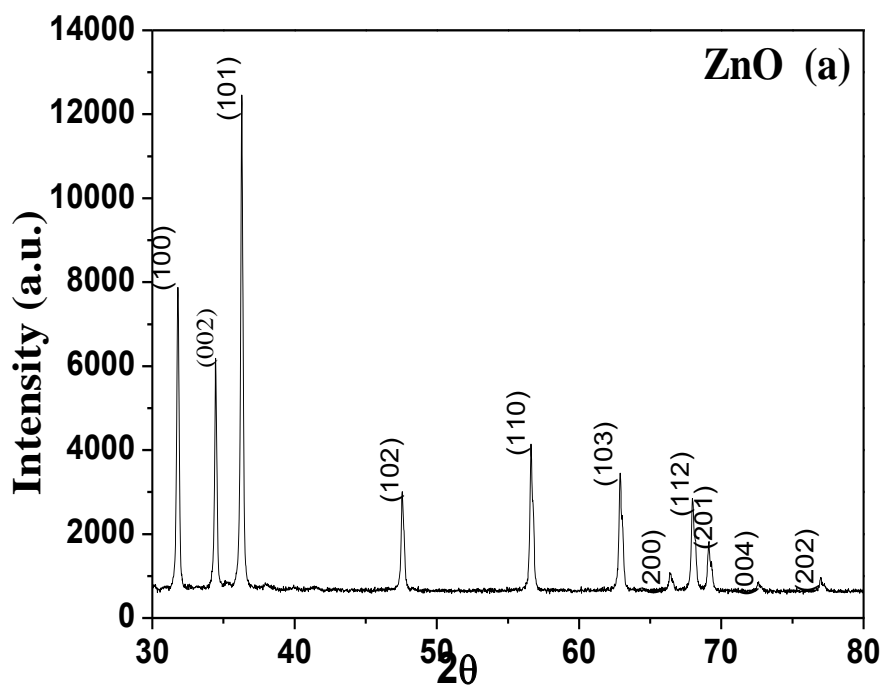
The nanoparticles of Zinc Oxide (ZnO) were synthesized first by using chemical wet technique. The Zinc acetate dehydrate, CTAB and NaOH were used for this method. A 2M solution of zinc acetate in de-ionized water was prepared. The surface properties were modified by adding 0.1g of CTAB to the prepared solution. Then a solution of NaOH was prepared in de-ionized water. This NaOH solution is added drop by drop to the previously prepared solution of zinc acetate and CTAB until white precipitate is formed. This white precipitate is then washed several times with the ethanol. It is then dried in oven at around 80°C and finally annealed at 400°C. The nanoparticles of pure ZnO were thus formed.

The core-shell structured nanoparticles composites of ZnO with PS were then prepared by performing direct in situ polymerization of methylmethacrylate and styrene monomers respectively with the mixing the ZnO nanoparticles simultaneously. In this process, first we mix ZnO nanoparticles in methyl meth acrylate monomer in the presence of toluene as reaction medium. Then 1% Benzoyl Peroxide was added to the solution to initiate the polymerization. The solution was continuously stirred for 30 min. at 80°C. The optimized viscous solution is used for obtaining thin films with the help of spin coating technique on glass substrate. The same procedure is followed for making ZnO-PS films also[16].

3. Characterization Techniques

3.1 X-Ray Diffraction (XRD) analysis

X-Ray diffractometer with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$) was used for obtaining diffractograms of the as prepared ZnO nanoparticles, pure PS thin film and ZnO-PS core-shell Structured Nanoparticle thin film at room temperature. The XRD pattern of ZnO nanoparticles shows peaks at 33.82° (100), 36.76° (002), 48.58° (102), 58° (101) and 60.86° (110) 2θ values (Figure 1(a)). Fig.3.5 (b) and (c) represents the XRD



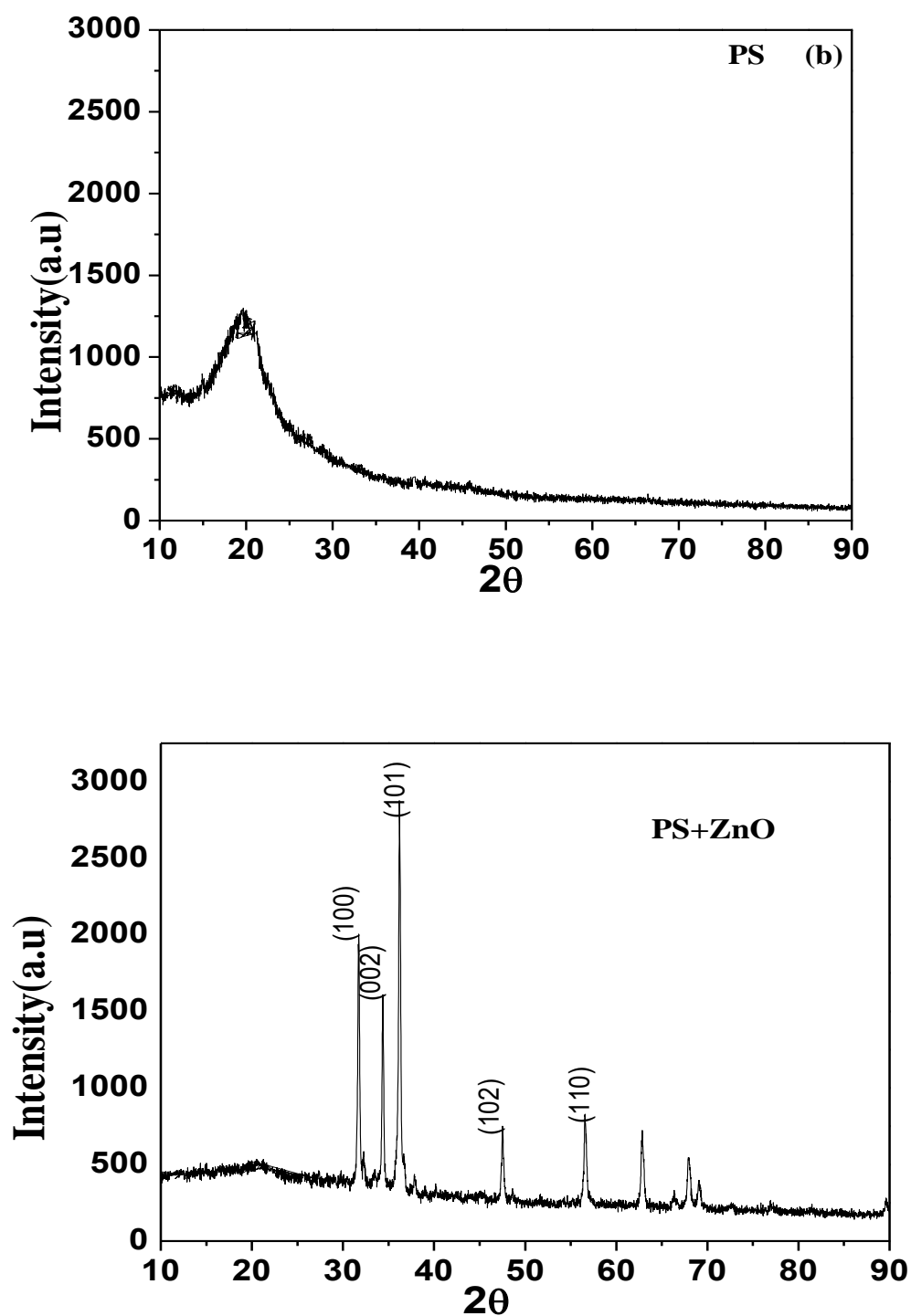
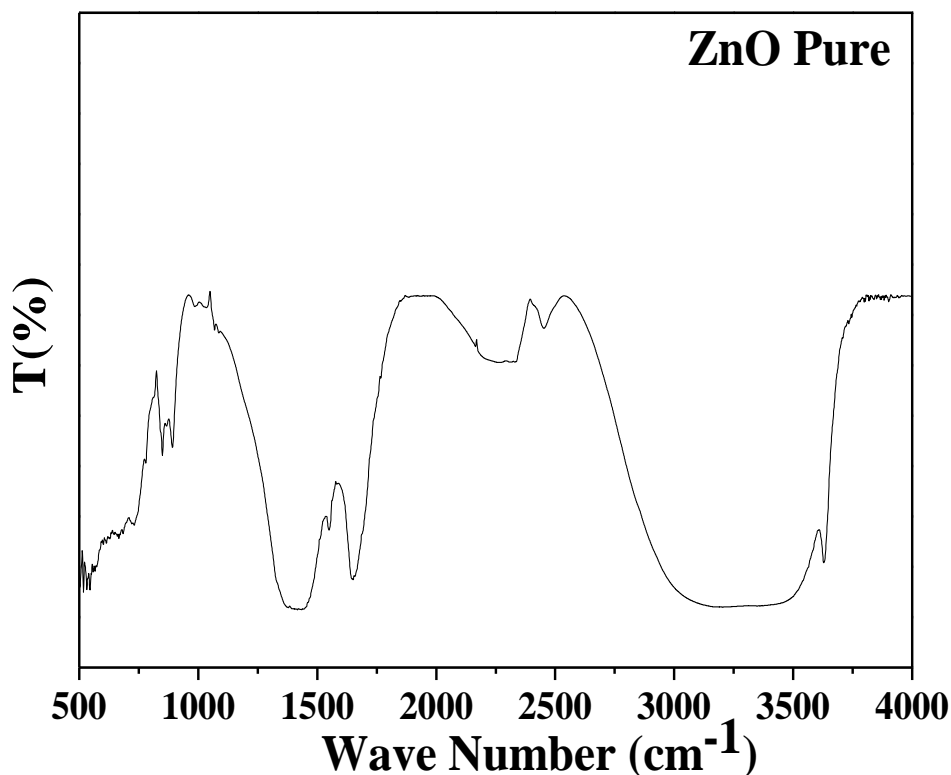


Fig 1: The XRD pattern of (a) Pure ZnO nanoparticles (b) Pure PS thin film (c) ZnO-PS thin film

plots of polystyrene (PS) and ZnO-PS nano-composites respectively. The patterns of ZnO-PS show a broad, non-crystalline (amorphous) peak of Poly-Styrene, as well as, the crystalline diffraction peaks of ZnO. The embodiment of ZnO in the polystyrene produces neither any new peak nor any shift in peak positions which clearly points out that the Core-shell structured system made by ZnO and PS consists of only two-phases [15]. The crystallite size of ZnO and PS-ZnO was found to be 15nm 15.10 nm corresponding to 101 plane. The high intensity XRD peaks of PS-ZnO was found corresponding to (100) and (101) planes.

3.2 FTIR Spectroscopy

Figure 2 shows the FTIR spectra of ZnO, PS, and ZnO/PS Core-shell nanocomposite. The FTIR plot of the nanocomposites clearly exhibits the characteristic absorption bands corresponding to polymeric groups present in PS and ZnO [21-23] as shown in table 1 below.



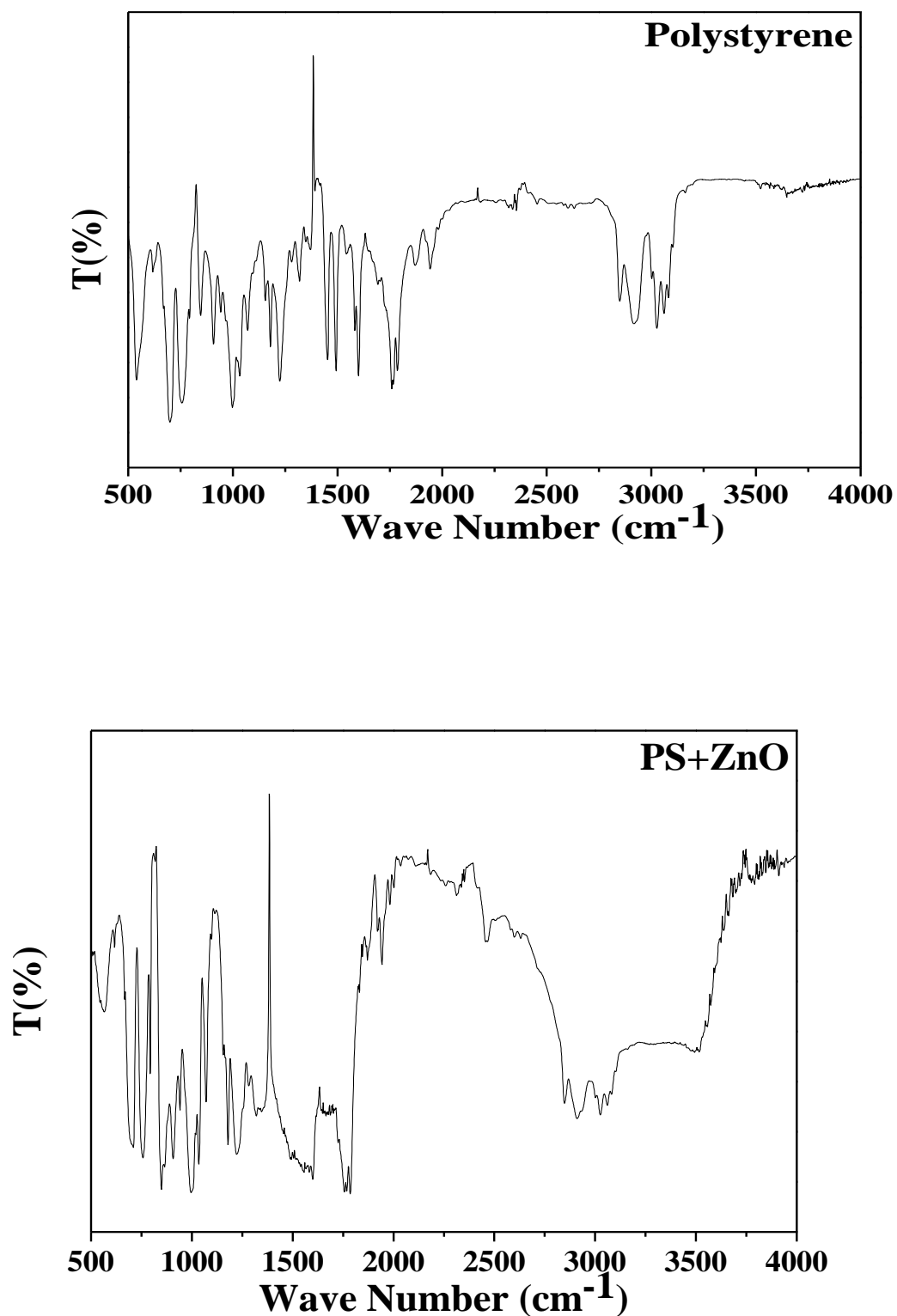


Fig.2: FTIR Spectra of (a) Pure ZnO nanoparticles, (b) Polystyrene (PS) and (c) Nanocomposite of Polystyrene and ZnO nanoparticles

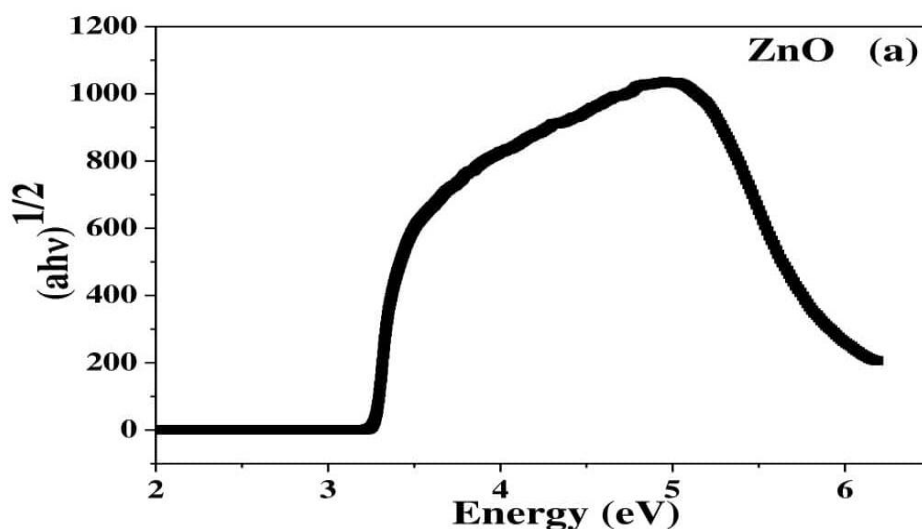
Table 1: The Bands Observed in FTIR Investigations and Corresponding Vibrations in ZnO-PS Core-shell Nanocomposite

Positons(cm^{-1})	Functional Groups
1450	CH_2 Stretching
1646.00	Due to Zn-O Stretching
1943-1725	Due to Asymmetric and symmetric vibration of methylene group of CH_2 of aliphatic carbon
2800-3000	Due to C-H aromatic tension
Above 3400	OH Stretching vibration

The shifts of infrared bands for PMMA in the hybrid film should be attributed to strong coulombic interaction between ZnO[16,17] and polymeric matrix. Zn-O bond is also present given by the peak in the region $\sim 1646\text{cm}^{-1}$. FTIR peaks at around $1943\text{-}1725\text{ cm}^{-1}$ is due to asymmetric and symmetric vibration of methylene group of CH_2 of aliphatic carbon. Peaks at $2800\text{-}3000\text{cm}^{-1}$ confirmed the presence of of C-H aromatic tension in the sample.

3.3 UV-Vis Spectroscopic Analysis:

Th Core-shell nanocomposite films obtained from UV-Vis spectrophotometer are demonstrated in fig. 3. The presence of polystyrene obviously modifies the absorption



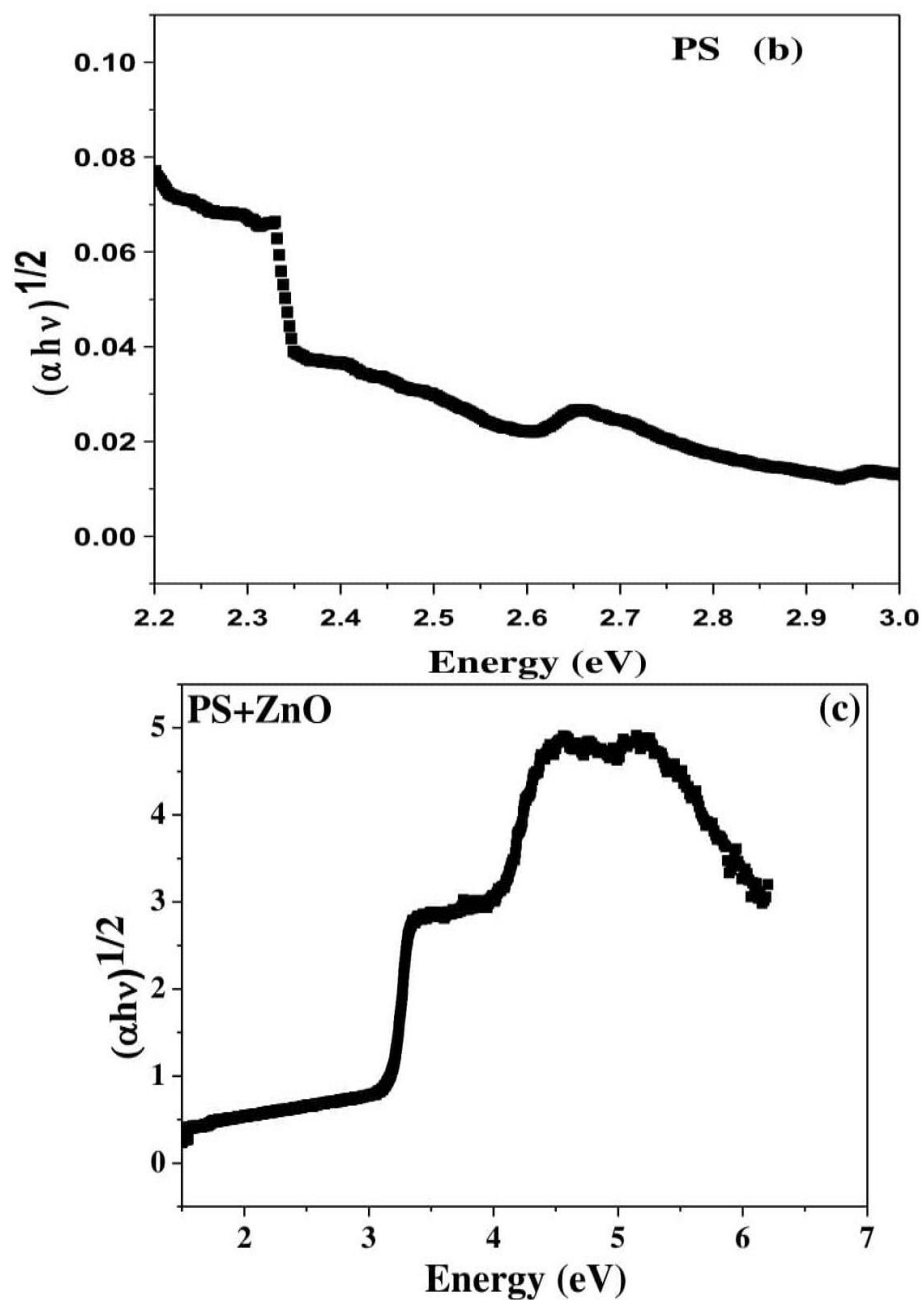


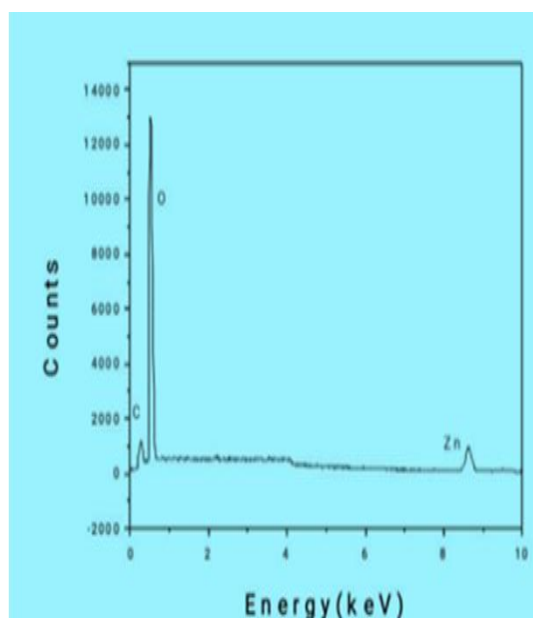
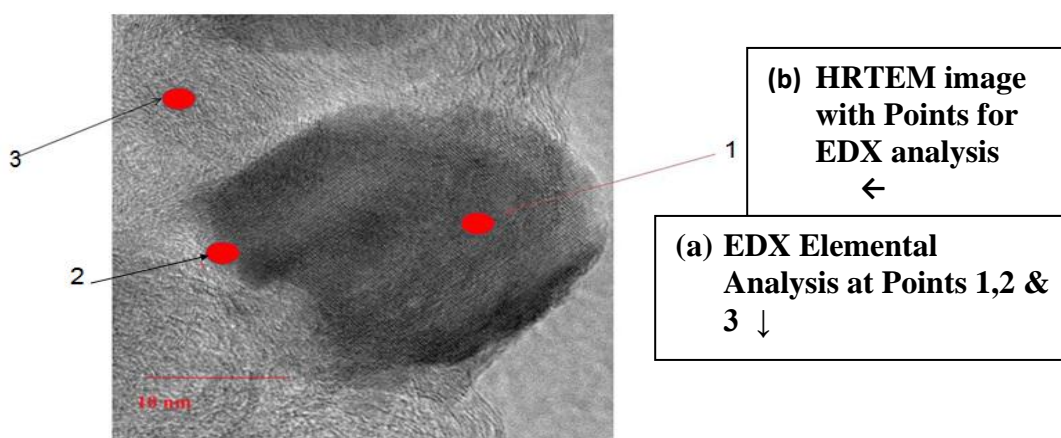
Fig. 3: UV-Visible spectra (a) Pure ZnO Nanoparticles (b) Pure PS (c) ZnO-PS nanoparticle thin film.

characteristics of nano ZnO. The UV absorption capacity of the ZnO/PS Core-shell nanocomposite films is appreciably found to improve [24]. The band gap also gets Tauc's plots i.e. absorption spectra of pure ZnO, Pure PS and ZnO-PS reduced with the reinforcement of ZnO

nanoparticles in polymeric matrix of PS that makes this nanocomposite material suitable for UV protectors [18,19].

3.4 HRTEM and EDX Analysis:

HRTEM studies on the ZnO/PS Core-shell nanoparticle composites showed that average particle is 21.7 nm. The microstructure is having three easily distinguishable regions i.e. ZnO particle (point 1), interfacial region (point 2) and polymer matrix (point 3) as shown in figure 4.



Element	Weight%	Atomic%
CK	15.20	22.42
OK	64.50	72.31
ZnK	20.30	5.27
Totals	100.00	

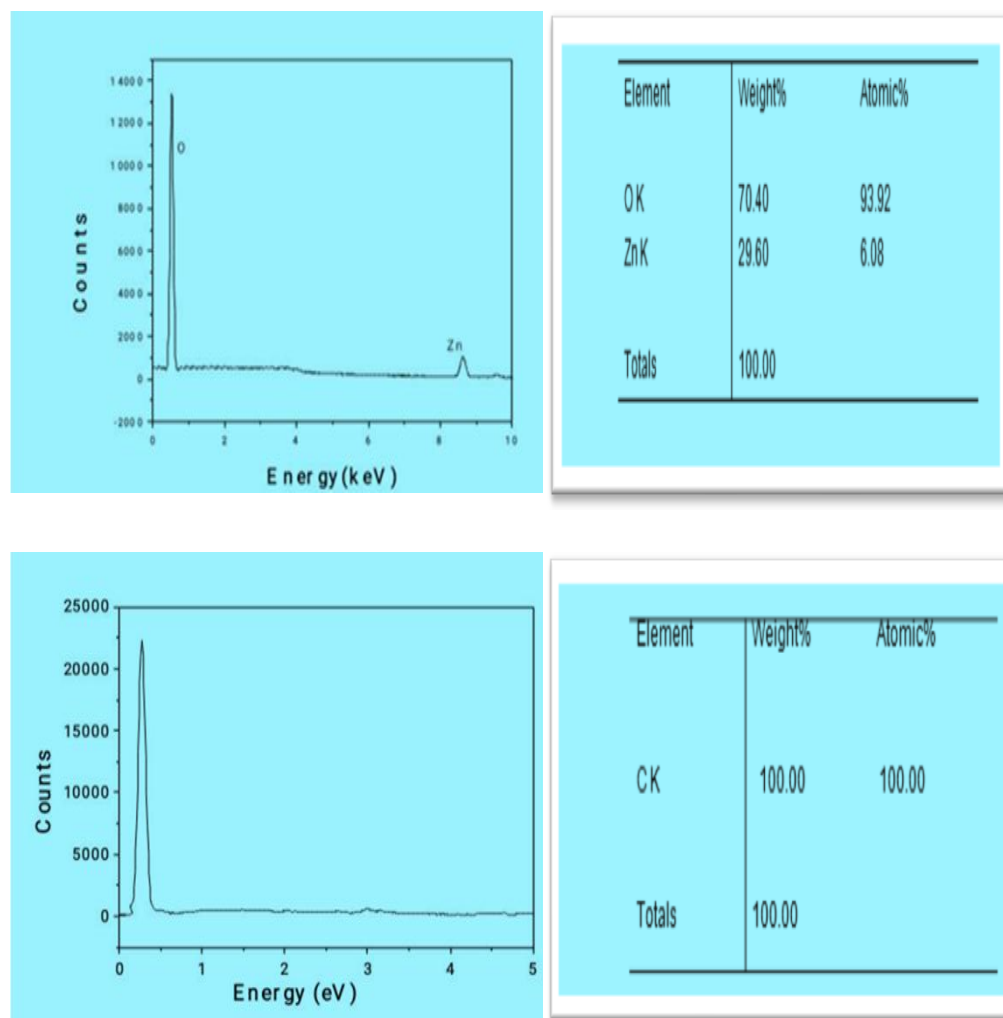


Fig. 4: (a) HRTEM image with Points for EDX analysis, (b) EDX Patterns and Elemental Compositions at three different points of HRTEM image of ZnO/PS Core-shell Nanocomposite Thin film

The EDX elemental analysis at these aforesaid three points revealed that point 1 and 3 are prominently having Zn and C respectively, whereas point 2 is having elemental composition altogether different from other two locations 1 and 2[20,21]. This clearly established that the core nanoparticle of ZnO is surrounded by an interfacial region of different composition from both the nanoparticle, as well as, the polymeric matrix. The Particle size as found by TEM image is 21.7 nm.

Conclusions

The Core-shell structured nanoparticles of ZnO-PS were successfully synthesized in PS matrix by wet chemical method through in situ polymerization of styrene monomers in a solution containing freshly prepared ZnO nanoparticles and transparent thin films of these nano-hybrids were coated on glass substrates by using spin coating technique. The XRD spectra of ZnO nanoparticles demonstrates a series of characteristic peaks that were in accordance with the XRD pattern of wurtzite phase, hexagonal ZnO structure. The crystallite sizes in ZnO, and ZnO/PS, corresponding to 101 plane, are found to be 15 nm, and 14.70 nm respectively.

- The nano crystalline character of the synthesized ZnO sample was verified by analysis of HRTEM and XRD. The core-shell structure is clearly evident from the EDX analysis of HRTEM images of the synthesized samples and elemental composition from EDX spectra is found to be close to expected one. The FTIR spectrum of the prepared nanocomposite samples exhibited the characteristic absorption bands corresponding to various groups present in polymeric matrix phase and ZnO which establishes the formation and phase integrity in the synthesized nanocomposites. The energy band gap of ZnO nanoparticles is found to be 3.22 eV, calculated by the Tau's plot of the UV-Vis absorption spectra. The polymer (PS) with ZnO nanoparticles totally alter the optical properties of ZnO nanoparticles and decreases the optical band gap. The ZnO/Polymeric nano composite thin films displayed good amount of UV protecting properties. This feature facilitates the applications of the ZnO-polymeric nanocomposite films as UV protectors or UV shielding.

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