Synthesis of Core-shell structured Zinc Oxide-Polymethylmethacrylate (PMMA) Films through Wet Chemical Method

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Abstract:

Zinc Oxide-Polymethylmethacrylate (ZnO-PMMA) core shell structured nanoparticles with inorganic core and the polymer shell were prepared successfully. ZnO has been selected in the present study for preparing the core shell nanoparticles in PMMA matrix for obtaining the UV-protection and high degree of transparency of the synthesized films in visible region. The outer surface of ZnO nanoparticles was initially modified by Cetyl Trimethylammonium Bromide (CTAB) to inhibit the agglomeration of ZnO nanoparticles and promote their compatibility with PMMA. The ZnO-PMMA nanoparticles films, prepared by Spin Coating Technique, were then characterized by X-ray Diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM), Fourier Transform Infrared Spectroscopy (FTIR) and UV–Visible Absorption Spectroscopy to study their structural, micro-structural and optical properties. The synthesized films demonstrate UV–Absorbing capacity and good amount of optical transparency in the visible-wavelength region.

1. Introduction

Core-shell nanoparticles are a class of dual phase particles with nano-dimensions. These have received a greater attention recently because of their outstanding and remarkable properties and numerous applications in medical, bio-technology, bio-imaging, gene screening or as catalyst. A number of core-shell nanoparticles can be synthesized by sensibly changing the cores, as well as, shells of the materials that show shows interesting properties with regards to the aforesaid applications. A variety of methods have been developed to prepare various types of core -shell nanoparticles, like Sol-gel method, Solvo-thermal method, Synthetic method of linking surfactants, Core Shell Emulsion Polymerization etc [1]. The present investigation is based on the synthesis of polymethylmethacrylate (PMMA) based films having a high transparency over all the visible range and be capable of powerfully absorbing the deep wavelengths of ultraviolet radiations. A number of nano-phase fillers, mainly the ceramic oxides like TiO_2 and ZnO can be added in the transparent PMMA to realize the selective absorption of specific range of electromagnetic spectrum [2]. Zinc oxide (ZnO), an interesting ceramic oxide with wurtzite structure having lattice parameters of a = 0.325 nm and c = 0.521 nm, has a wide band gap of 3.4 eV and high binding energy of 60 meV. Because of its attractive features, this material finds a number of applications; such as in transparent electronics, for treatment of various skin diseases, as sensors, ultraviolet (UV) light emitters and for spin electronics [3-10].

ZnO can synthesize in various shapes and particle sizes and by various synthetic approaches. Out of these, chemical processes are very efficient for preparation of nanoparticles with different sizes in large quantities [3]. However, ZnO nanoparticles agglomerate very eagerly that brings in the instability in macroscopic properties of this material. In addition to this problem, the water vapours present in the atmosphere are also liable to get adsorbed on the surface of ZnO particles, resulting into the fluorescence quenching effect. Many efforts have made to protect ZnO nanoparticles from aggregation and adsorption effects. Among all sorts of strategies, coating ZnO with polymer is a better choice for the reason that the cross-linked polymer be able to figure a rigid shell around the ZnO core, which is hard to be removed. To attain stable ZnO-PMMA films, modifications of the surface of ZnO nanoparticles with binding agents are very much essential, so that agglomeration of ZnO nanoparticles can be prevented.

We know that Polymethylmethacrylate (PMMA) is an amorphous transparent thermoplastic material, which is used as an alternate to inorganic glass, as it undergoes a ductile fracture to a certain extent than brittle one. Therefore, PMMA can be easily processed, moreover, it also exhibits a higher impact strength as compared to glass [11]. The nanoparticles of ZnO embedded in PMMA matrix may have potential applications in non-reflection coatings, protecting films from UV radiations, transparent protective layers, as well as, barrier layers for slowing down the spread of fire [12].
Despite the promising application potential, development of a simple and efficient method for synthesis of polymer clad ZnO nanoparticles embedded in PMMA matrix still remains a challenge because of compatibility related issues of this nano-ceramic material with the polymeric matrix and certain processing stage troubles [13]. For the preparation of uniform ZnO-PMMA nanoparticles, it is critical to attain good dispersion stability [14]. The present paper reports on an innovative method as a solution

to the aforesaid problems by preparation of surface modified ZnO-PMMA core shell structured nanoparticles in PMMA matrix via Wet Chemical Synthesis method.

2. Experimental

2.1 Synthesis of ZnO nanoparticles:

ZnO nanoparticles were prepared by using chemical wet method. Zinc acetate dehydrate (Zn (O2CCH3)2(H2O)2), Cetyl Trimethylammonium Bromide (CTAB) and sodium hydroxide (NaOH) were used as starting materials. First the 2M solution of zinc acetate with de-ionized water was prepared. Then 0.1g of CTAB is added to this solution for modifying its surface properties. A solution of NaOH was also prepared separately in deionized water and it is added to the previously prepared solution of zinc acetate and CTAB drop by drop until a white precipitate is formed. The white precipitate so obtained was then washed with the ethanol several times and then dried followed by annealing at 4000C. The nanoparticles of pure ZnO were thus obtained.

2.2 Synthesis of PMMA and ZnO-PMMA Core-shell nanoparticles :

A pure PMMA sample was synthesized by the polymerization of monomer Methyl Methacrylate (MMA) in the presence of Benzoyl Peroxide as initiator and distilled water as reaction medium. The core-shell nanoparticles of ZnO with PMMA were prepared by performing in situ polymerization of methylmethacrylate monomer with the mixing of ZnO nanoparticles simultaneously. In this process, initially the as prepared ZnO nanoparticles were mixed in methylmethacrylate 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 mins at 80ºC to get an optimized viscous solution suitable to be used for the spin coating technique to deposit thin films on glass substrate.

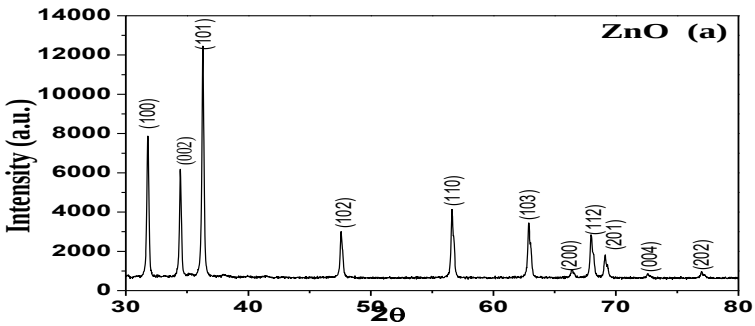
2.4 Characterization:

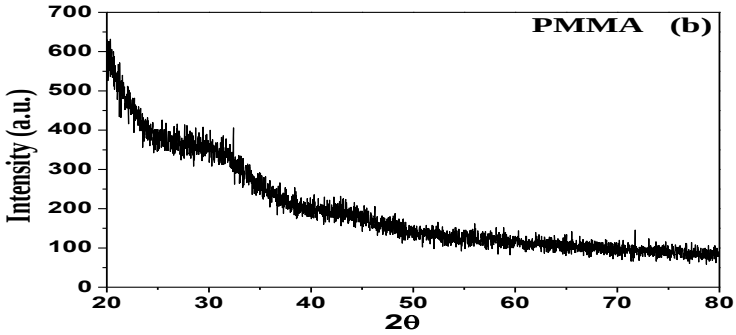
Powder X-Ray diffractometer (Bruker) was used for recording the X-Ray Diffraction (XRD) patterns of the as prepared ZnO naoparticles, pure PMMA and core shell ZnO nanoparticles in PMMA matrix at room temperature by using the CuKα radiation (λ = 0.1542 nm) and operating the equipment at 40 kV and 40 mA. The size of crystallite was estimated using the Scherer equation $L_{hkl} = (0.9\lambda)/(\beta \cos \theta)$ at the FWHM (full width half maximum) of the major peak of XRD. Transmission Electron Microscopy (TEM), FEI tencai T^2-20, microscope fitted with a LaB_6 filament, operated under accelerated voltage of 200 kV, was used for morphological characterization of samples. TEM grids used to prepare samples by dropping precursor solutions onto grids. The Fourier Transform-Infrared Spectroscopy (FTIR), (Perkin Elmer) is used to identify the the molecular components and structure of the samples. UV double beam spectrophotometer (UV 704SS) was used for obtaining UV–Vis absorption spectra of the ZnO-PMMA nanoparticles.

3. Results and Discussions

The X-Ray Diffraction (XRD) patterns of the as prepared ZnO naoparticles, pure PMMA and core shell ZnO nanoparticles in PMMA matrix at room temperature are shown in Figure 1(a). XRD pattern of as prepared ZnO nanoparticles shows a series of characteristic peaks at 33.82° (100), 36.76° (002), 48.58° (102), 58° (101) and 60.86° (110) that are in accordance with the XRD pattern of wurtzite phase, hexagonal ZnO structure. This particular phase has lattice constants a and c of 3.25 Å and 5.21 Å, respectively. The average crystal size of ZnO nanoparticles was 7 nm, as calculated from Scherrer's formula.

In figure 1(b) a broad hump observed revealing the presence of PMMA as an amorphous polymer. In figure 1(c) the XRD of ZnO-PMMA is shown. The ZnO peaks have been observed on the amorphous background. It confirms the presence of ZnO and PMMA phases in the thin films.





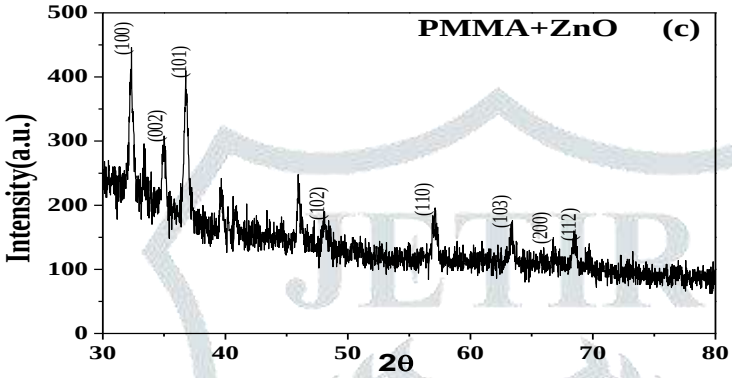
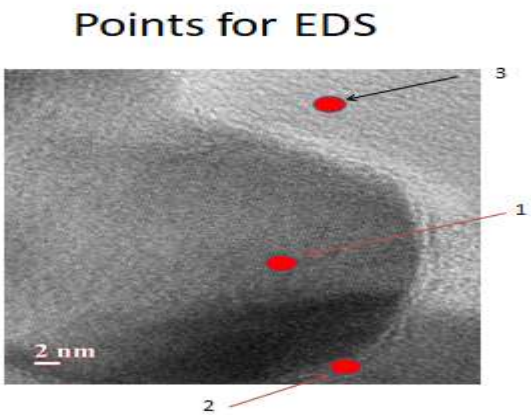
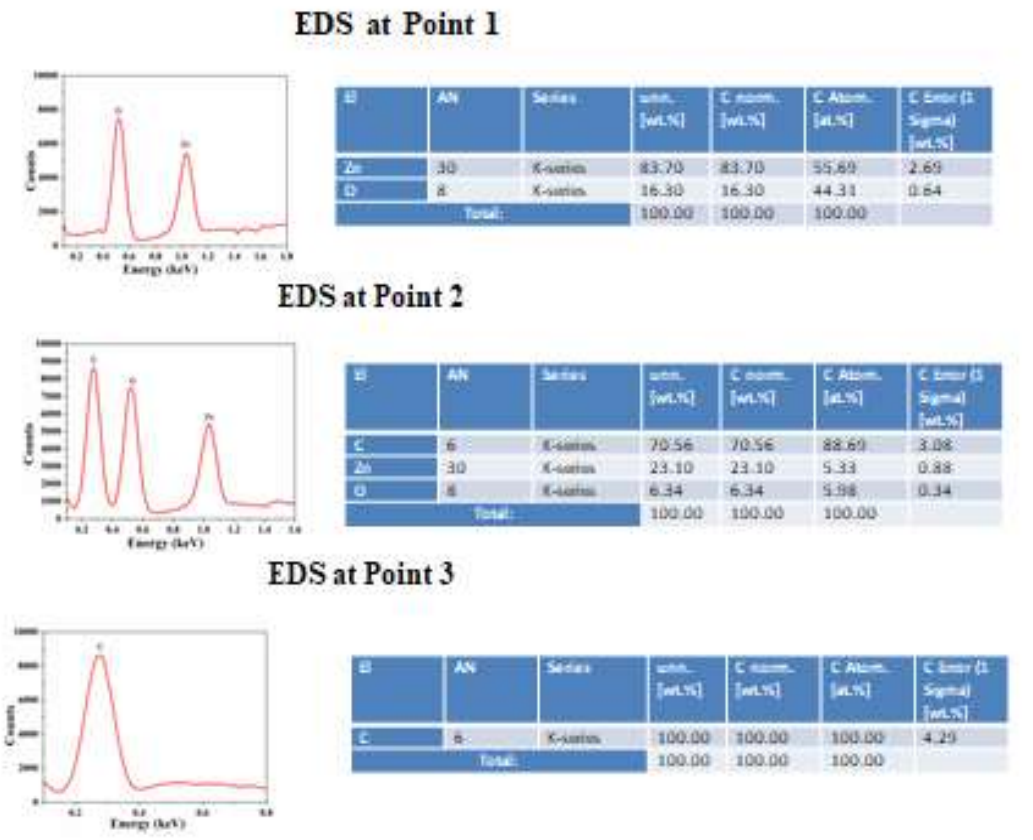


Fig.1: XRD Pattern of (a) Pure ZnO nanoparticles (b) Pure PMMA (c) ZnO-PMMA nanoparticles

The HRTEM images of the ZnO-PMMA nanoparticles are shown in Fig. 2. The image clearly indicates the presence of core shell like structure of the nanoparticles. To confirm this result, the Energy Dispersive X-ray Spectroscopy (EDS) was performed at three different locations 1, 2 and 3 on HRTEM image. Position 1 represents location of the oxide nanoparticles. The position 2 indicates the boundary of nanoparticle and polymer (PMMA) whereas position 3 represents the location on polymer. It is clearly noted the centre part of this nanoparticles contains only Zn and O elements however outside this surface, EDS shows only carbon (C) which represent the polymer. In nutshell, core shell like structure is evident from this study.





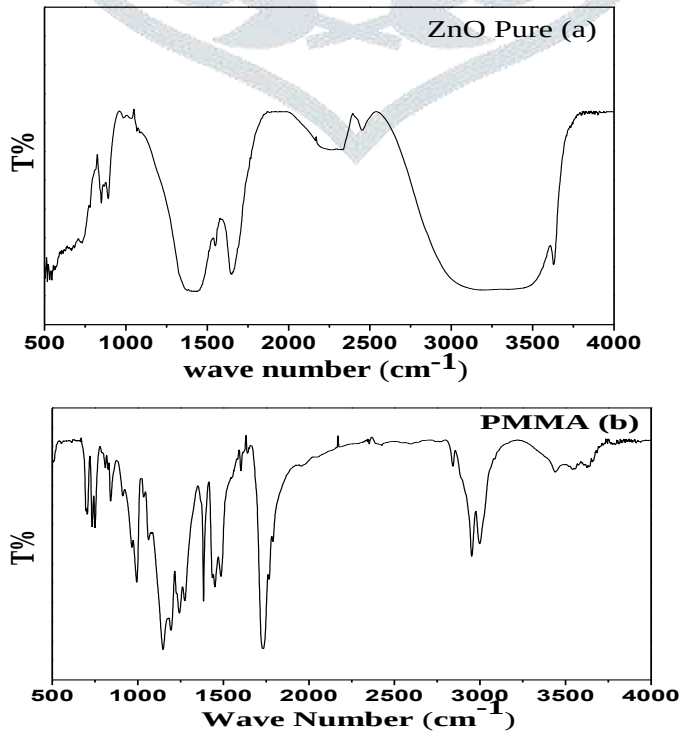
El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
Zn	30	K-series	83.70	83.70	55.69	2.69
O	8	K-series	16.30	16.30	44.31	0.64
Total:			100.00	100.00	100.00	

El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
C	6	K-series	70.56	70.56	88.69	3.08
Zn	30	K-series	23.10	23.10	5.33	0.88
O	8	K-series	6.34	6.34	5.98	0.34
Total:			100.00	100.00	100.00	

El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
C	6	K-series	100.00	100.00	100.00	4.29
Total:			100.00	100.00	100.00	

Fig. 2: EDS Pattern of HRTEM Image of ZnO-PMMA Nanoparticles Thin Film at 03 Different Points

Fourier Transform Infrared (FT-IR) Spectra of the samples, obtained with Perkin Elmer spectrophotometer in the wave number range 400-4000 cm^{-1} clearly exhibits the characteristic absorption bands corresponding to polymeric groups and ZnO. The Fourier Transform Infrared Spectra of the pure ZnO nanoparticles, PMMA and ZnO -PMMA nanoparticles are shown in Fig. 3.



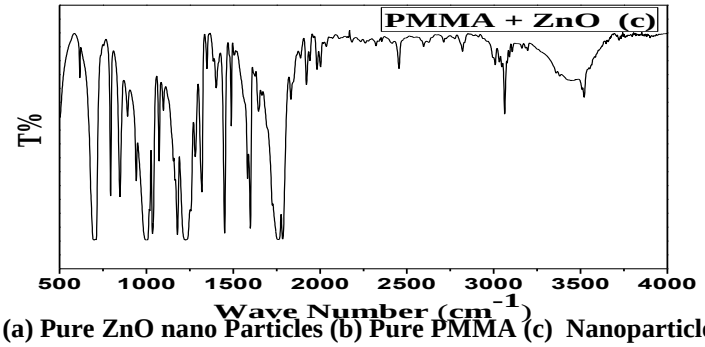


Fig. 3: FTIR Spectra of (a) Pure ZnO nano Particles (b) Pure PMMA (c) Nanoparticles of ZnO-PMMA

The figure clearly reveals that all the bands are indexed with their corresponding compounds. These bands confirm the presence of ZnO- PMMA nanoparticles. The bands observed in FTIR investigations and corresponding vibrations are given in the table 1 below.

Table 1: The Bands Observed in FTIR Investigations and Corresponding Vibrations

Wave Number (cm^{-1})	Vibration Mode
1478	CH_2 Stretching
1646.00	Due to Zn-O Stretching
1725	Due to free Carbonyl C=O Stretching
2845.59-2960.26	Due to Asymmetric and symmetric vibration of methylene group of CH_2 of aliphatic carbon chain
Above 3400	OH Stretching vibration either from water or hydroxyl terminated compounds, Silicates or N-H stretching vibration either from urea or amino group

A broad absorption centered in the range 3400-3550 cm^{-1} was observed for all thin films and is assigned to –OH stretching. The strong absorption C=O stretching peak of PMMA is at ~1725 cm^{-1}. All the composite films exhibit the characteristic absorption peaks of ~ 1725- 1732 cm^{-1} and ~ 2950 cm^{-1} which are caused by the stretching vibration bands of C=O and C-H bonds in the PMMA segments respectively. The absorbance at ~1478 cm-1 and ~ 2800-3000 cm^{-1} regions that are characteristic of CHx bending and stretching respectively. The Zn-O bond is shown the peak in the region ~ 1646cm^{-1}. Compared with the infrared spectra of the pure PMMA, each characteristic bond of ZnO -PMMA becomes stronger or weaker with little shifts. The shifts of infrared bands for PMMA in the hybrid film should be attributed to strong coulombic interaction between ZnO and polymeric matrix.

The Fig. 4 below represents the Tauc's plots $[(\alpha h\nu)^{1/2}$ vs. hv] of UV-Vis spectra of pure ZnO nanoparticles, thin films of pure PMMA and the ZnO-PMMA nanoparticles. As PMMA is a transparent polymer, nanoparticles of the ZnO-PMMA exhibit properties that are mixture of the properties of the ZnO and PMMA. It is clear from the Fig. 4 (a) that ZnO has a clear absorption edge and the energy band gap of ZnO nanoparticles is found to be 3.22 eV. Pure PMMA is found to have clear absorption bands as depicted in Fig. 4 (b). These bands, present in in the UV-Visible region, show the presence of different functional groups. As shown in Fig. 4 (c), the UV-Vis plot of the ZnO-PMMA nanoparticles is totally different from that of pure PMMA and ZnO nanoparticles which clearly indicate that the core shell nanoparticles of ZnO in PMMA have entirely different optical properties as compared to ZnO nanoparticles and PMMA with fairly high UV absorption and high degree of transparency to the visible radiations.

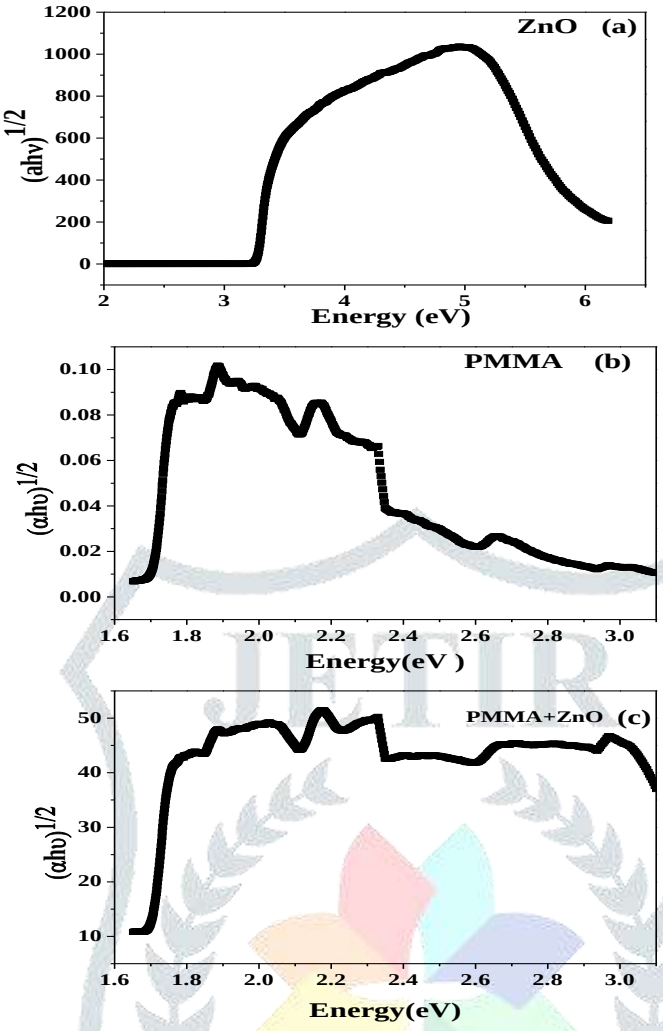


Fig. 4: UV-Vis spectra of (a) Pure ZnO Nano particles (b) Pure PMMA (c) ZnO-PMMA nanoparticle thin film.

Conclusively, a transparent visible and UV-Protecting ZnO nanoparticles based PMMA film is developed by a novel and simplified wet chemical technique. The XRD results revealed that the ZnO-PMMA nanoparticles presented simultaneously the amorphous nature of PMMA and crystalline structure of ZnO. The core-shell structure of the prepared nanoparticles has been demonstrated by the HRTEM. The FTIR and UV results clearly show that the thin films produced have a good amount of UV absorption and apparently good transparency to visible radiation.

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