Structural and Optical Properties of Magnesium Oxide Core-shell Structured Nanoparticles with PMMA Matrix

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Abstract

The Core-shell structured nanoparticles of magnesium oxide (MgO) with polymethylmethacryaltate (PMMA)polymer were synthesized. The synthesis process proceeds by means of polymerization of Methyl Methacrylate (MMA) monomer on the surface of nanoparticles of MgO after modification by the surface-active agent Cetyltrimethylammonium Bromide (CTAB). Benzoyl Peroxide was used as initiator to attach PMMA on the surface of CTAB-modified magnesium hydroxide. The thin film of hybrid nanoparticles of MgO-PMMA were prepared by spin coater on the glass substrate. Spectroscopic tools such as Fourier Transform Infrared Spectroscopy (FTIR) and UV–Visible Absorption Spectroscopy were used to study the optical properties of the hybrid thin films. X-ray Diffraction (XRD) and High Resolution Transmission Electron Microscopy (HRTEM) techniques were used to investigate the structural properties of the hybrid thin film. The results demonstrated that the PMMA, can be efficiently coupled to the surface of the magnesium hydroxide nanoparticles modified with CTAB, which significantly improve the dispersibility and compatibility of the nanoparticles in this organic phase.

1. Introduction

The synthesis of Core-shell nanoparticles with the core of inorganic material and the polymeric shell has attracted much attention due to the dual properties of core and shell materials [1-3]. The nanoparticles in general, which are formed by the amalgamation of core and shell particles, improve the properties of the product, which can significantly increase the region of applications in various fields [4]. Until then, many attempts have been made to synthesize the core-shell structured nanoparticles by various methods such as SnO_2, SiO_2, CeO_2 or Fe_2O_3 and many more [5-8]. The synthesized core-shell nanoparticles always show different properties than the individual particles [9].The foremost difficulty with the making of core-shell structured nanoparticles is the ability to create the polymer coating on the nanoparticles surface without affecting the nature of nanoparticles, through the solution phase mechanism of polymerization. Controlling the rate of polymerization is the key issue in coating the surface of nanoparticles. To achieve this goal, several methods have been developed to coat the surface of nanoparticles by the polymer shell, which includes layer-by-layer approach, different types of polymerization mechanisms [10-13], and particle bound initiators.

The synthesis of core-shell structured nanoparticles of MgO core and PMMA shell is of great interest as Magnesium oxide (MgO) is a category of the practical semiconductor metal oxides, which is widely used as catalyst and as optical material. PMMA is one of the most promising polymers, which used in diverse areas, having good conductivity, easily synthesized and with good stability in the environment.

Here, we report the synthesis of transparent core shell structured MgO-PMMA nanoparticles by chemical synthesis followed by in situ polymerization.

2. Experimental

2.1 Synthesis of MgO nanoparticles

The nanoparticles of MgO are synthesized using Magnesium Nitrate Hexahydrate [$Mg(NO_3)_2(H_2O)_6$], Cetyltrimethylammonium bromide (CTAB) and sodium hydroxide powder of AR grade of high purity. The deionized water and ethanol used as a solvent and for washing reagent in the chemical reaction. Initially the Magnesium Nitrate Hexahydrate of weight 5.21g (0.2 M) dissolved in 200ml of distilled water and CTAB solution. Then 0.8g (0.2 M) of NaOH has dissolved in 200 mL distilled water. Then 200 mL of NaOH solution is added in solution of [$Mg (NO_3)_2(H_2O)_6$] drop-wise till white precipitates were formed. Afterwards the solution was kept on table at rest for 2 hours so that, the precipitates were settled down at the bottom of the beaker. The white precipitates has filtered and washed using distilled water. The final product was kept in vacuum oven (Quality Make, India) at 80 °C for 4 hours. The final powder was then calcined at 400°C for 3 hours for phase formation. The final product after calcination was a fine nano sized particles of MgO.

2.2 Synthesis of PMMA and MgO -PMMA nanoparticles: The pure samples of PMMA were synthesized by the polymerization of Methyl Methacrylate (MMA) monomer in the presence of Benzoyl Peroxide as initiator and toluene as reaction medium. The modified nanoparticles of MgO with CTAB were coated by the polymer PMMA by in situ polymerization of

methyl methacrylate (MMA) monomer in the presence of toluene as reaction medium. To initiate the polymerization mechanism of the monomer, aprox.1% benzoyl peroxide was added. The solution was stirred continuously for 30 mins at 80ºC. The resultant solution was used for making thin film on the glass substrate by using spin coater.

2.3 Characterization

The morphological investigation was carried out by the High Resolution transmission electron microscopy (HRTEM) by JEOL FEI Tencai T-20. The crystallinity and crystal phases were determined by X-ray powder diffractometer (Panalytical, XRD Xpert-3) with CuKα Radiation (λ=1.54178Å) with Bragg angle ranging from 30º to 80°. Samples composition of the synthesized magnesium oxide nanoparticle with polymer matrix was analyzed by the Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, spectrum-two) in the range of 400- 4000 cm^{-1}. UV double beam spectrophotometer (UV 704SS) was used for obtaining UV–Vis absorption spectra of the MgO-PMMA nanoparticles.

3. Results and discussion

X-Ray diffractometer with Cu Kα radiation (λ = 1.54060 Å) was used for obtaining the patterns of XRD (X-ray diffraction) at room temperature. The XRD pattern of MgO nanoparticles shows peaks as follows: 37.062° (111), 43.069° (002), 62.344° (022), 74.619° (113) and 78.443° (222) in Figure 1(a). The XRD pattern of MgO nanoparticles showed a series of characteristic peaks that were in accordance with the phase group of cubic MgO (Fm -3m). There are some other peaks indexed as star (*) observed which are in accordance with the phase group cubic MgO_2 (Pa -3m). This particular phases have lattice constants a=b=c=4.21 Å and 4.84 Å, respectively. In figure 1(b) a broad hump observed revealing the presence of PMMA as an amorphous polymer.
In figure, 1(c) the XRD of MgO-PMMA is shown. The MgO peaks have been observed on the amorphous background. It confirms the presence of MgO and PMMA phases in the composite thin films.

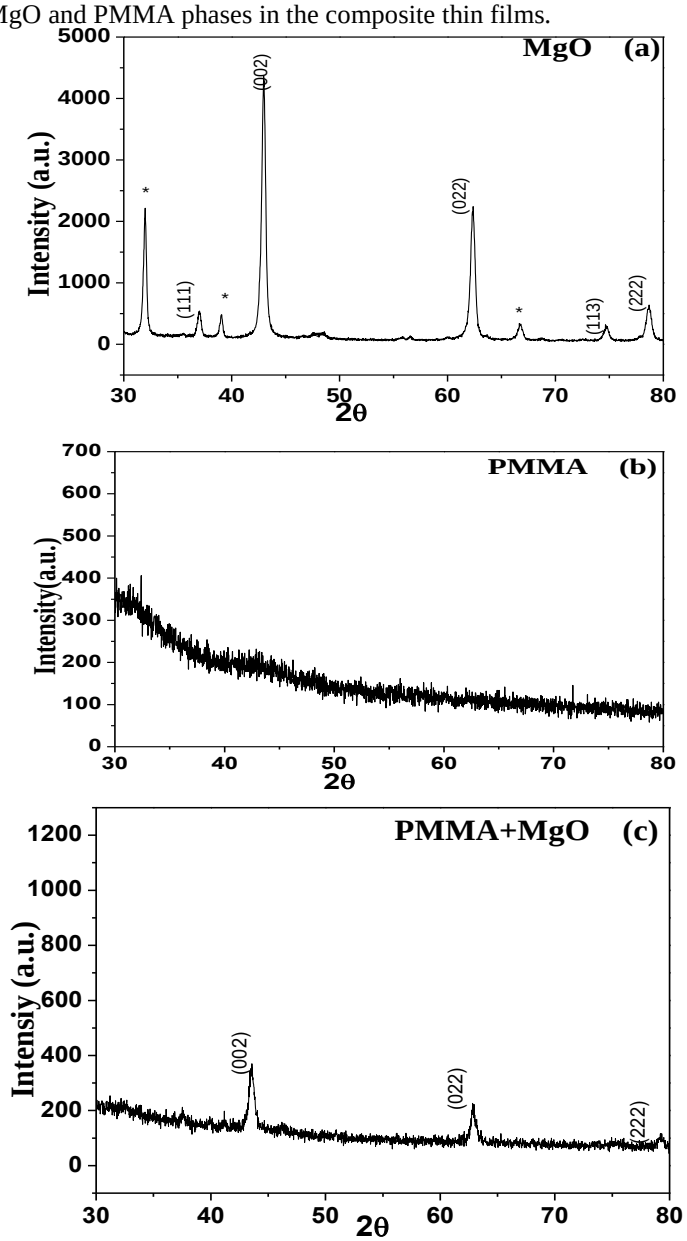
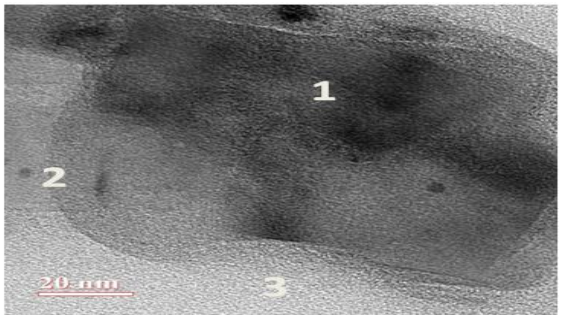
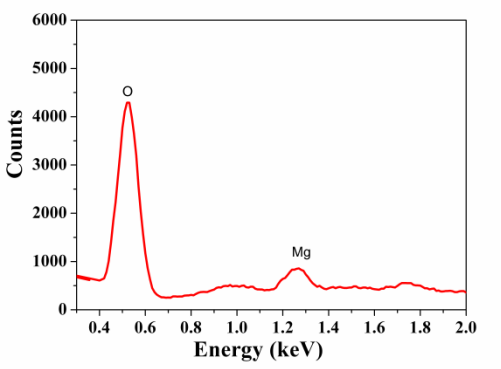


Fig.1. XRD Pattern of (a) Pure MgO nanoparticles (b) Pure PMMA thin film (c) Nanoparticles of MgO-PMMA

The Fig.2 represents the HRTEM images of the MgO-PMMA nanoparticles. The image evidently points out the core-shell type structure of the nanoparticles. The Energy Dispersive X-ray spectroscopy (EDS) was done to confirm the core-shell structure, at different positions 1, 2 and 3. Here the position 1 corresponds to point of the oxide nanoparticles. The 2nd position of the image signifies the edge of nanoparticle and polymer (PMMA) while position 3 characterizes the position on polymer. It is totally understood by the image that the centre part of this nanoparticles includes only Mg and O elements on the other hand, outside this surface, EDS illustrates only carbon (C) which represent the polymer. In nutshell, core-shell structure is marked from this study.

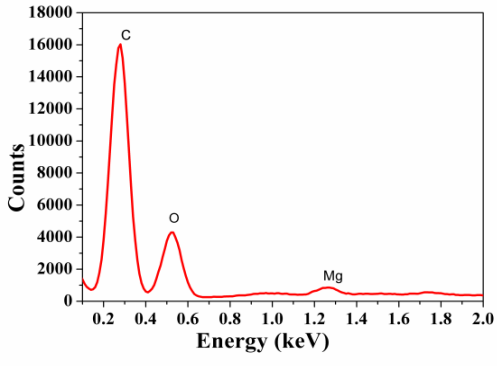


EDS spectra at point 1 (on the core of the particle).



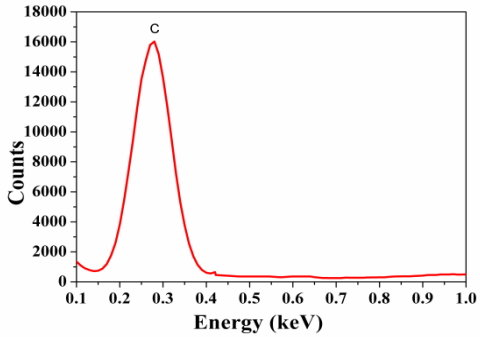
El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
Mg	12	K-series	55.45	55.45	45.04	2.50
O	8	K-series	44.55	44.55	54.96	2.61
Total:			100.00	100.00	100.00	

EDS spectra at point 2 (on the boundary of the particle and Polymer).



El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
C	6	K-series	92.11	92.11	95.04	3.66
Mg	12	K-series	4.38	4.38	2.23	0.22
O	8	K-series	3.52	3.52	2.72	0.23
Total:			100.00	100.00	100.00	

EDS spectra at point 3 (on the Polymer matrix).



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	4.82
Total:			100.00	100.00	100.00	

Fig.2: EDS Pattern of HRTEM image of MgO-PMMA nanoparticles thin film with three different points.

The Fourier transform infrared spectroscopy of the pure MgO nanoparticles, PMMA thin films and MgO -PMMA nanoparticles thin film are shown in figure 4. The figure noticeably reveals that all the bands in the spectrum are indexed with their corresponding compounds. All the bands representing MgO - PMMA are shown in the table below. These bands confirm the presence of MgO-PMMA. The mode corresponds to 867cm^{-1} represents the Mg-O stretching and deformation vibration. The bands and there vibrations are given in the table below.

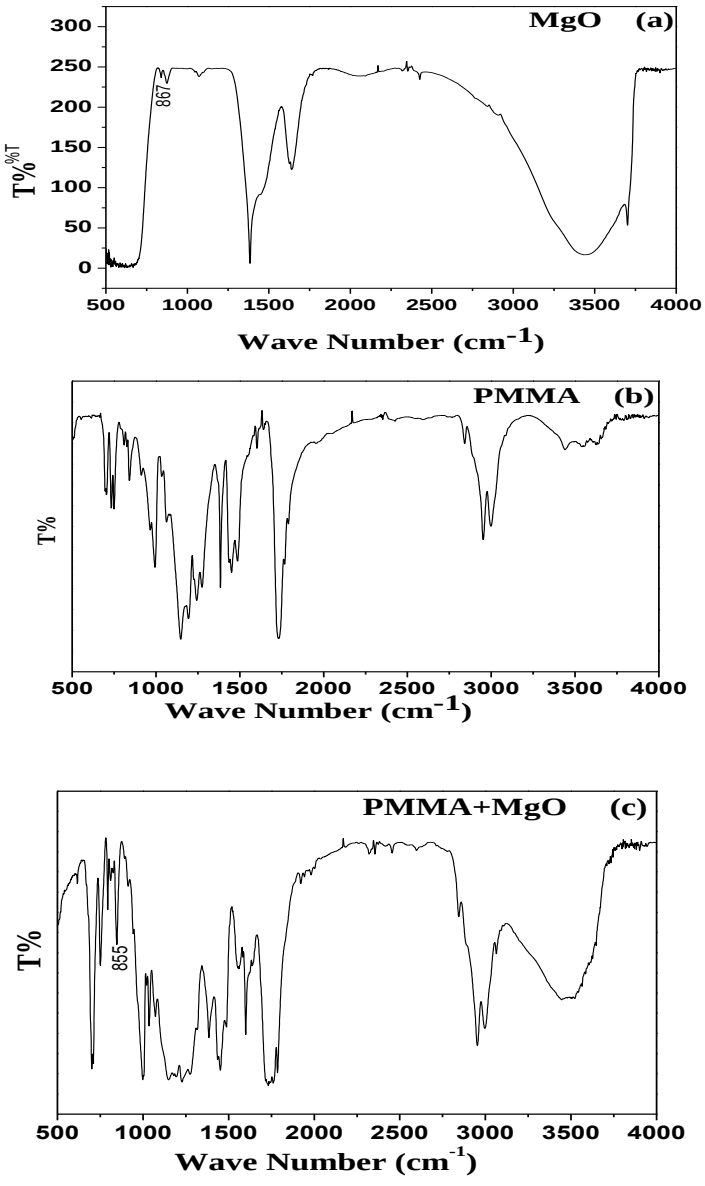


Fig.3. FTIR Spectra of (a) Pure MgO nano Particles (b) Pure PMMA (c) Nanoparticles of MgO-PMMA

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

1478	CH2 Stretching
867.00	Due to Mg-O-Mg Stretching
1725	Due to free Carbonyl C=O Stretching
2845.59-2960.26	Due to Asymmetric and symmetric vibration of methylene group of CH2 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

In the Fig.4, the Tauc's plots of $[(\alpha h\nu)^{1/2}$ vs. $h\nu]$ pure MgO nanoparticles, pure PMMA thin films and MgO-PMMA nanoparticles thin films are shown. As PMMA is a transparent polymer, when the nanoparticles of the PMMA- MgO is studied, a mixture of the properties of the MgO and PMMA has been observed. It is clear from the figure that MgO has a clear absorption edge and the energy band gap of MgO nanoparticles is found to be 5.36ev. As PMMA pure has absorption bands represents different functional group in the UV-Visible region. The energy band gap of MgO-PMMA composite decreases to 3.97 eV, which makes it suitable for photovoltaic and optical applications.

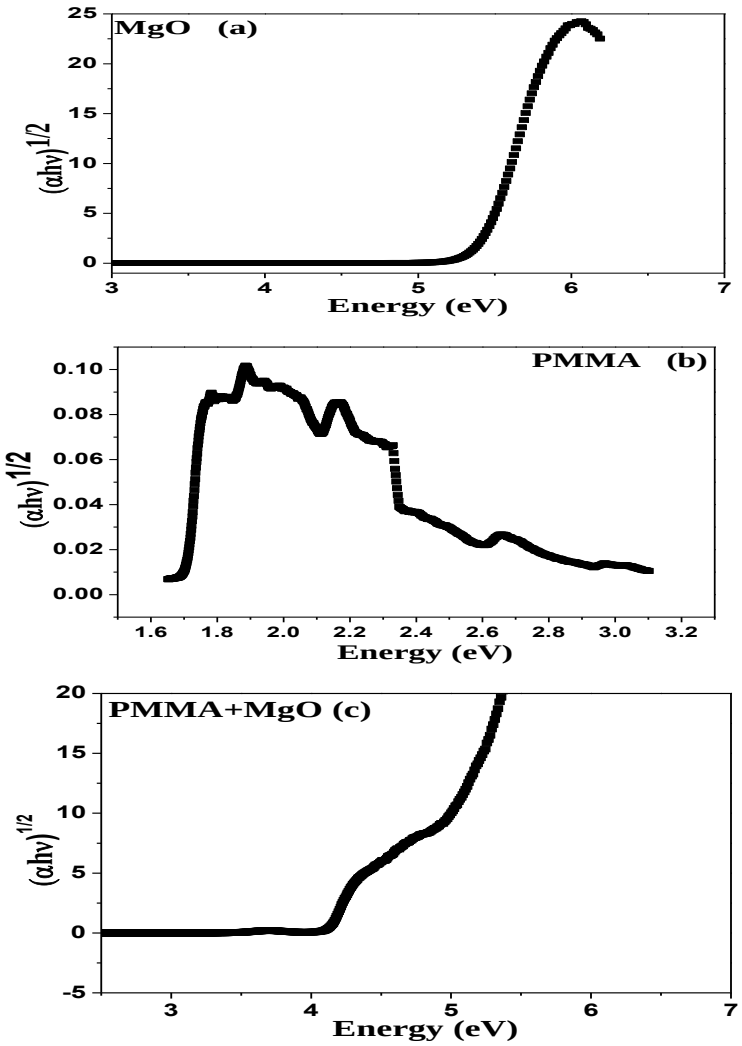


Figure 4: UV-Vis spectra of (a) Pure MgO Nano particles (b) Pure PMMA thin film (c) MgO- PMMA thin film.

Conclusion

MgO-PMMA transparent nanoparticles were prepared by a novel technique by in situ polymerizaton of MMA monomer. The influence of polymer matrix on the magnesium oxide nanoparticles were studied. The XRD results revealed that the MgO-PMMA nanoparticles presented simultaneously the amorphous nature of polymethylmethacrylate and crystalline structure of MgO powder. The MgO- PMMA nanoparticles are of Core -shell structured, depicted by HRTEM. The FTIR and UV results clearly show that the thin films produced have a good amount of transparency to visible radiation and low band gap of MgO-PMMA makes them suitable for optical applications.

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