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Optical nonlinearity of CdSe-PMMA hybrid nanocomposite investigated via Z-scan technique and semi-empirical relations

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ABSTRACT

CdSe-PMMA nanocomposite has been synthesized by ex-situ technique. The effect of different Ag doping concentrations on its structural and optical properties has been studied. X-ray diffraction reveals the hexagonal wurtzite structure of the polymer nanocomposites with preferential growth of the nanocrystals along (100) direction. Transmission electron micrograph shows the spherical CdSe nanoparticles embedded in polymer matrix. The nonlinear refractive index of the nanocomposites has been calculated using Tichy & Ticha semi-empirical relations and Z-scan technique. Z-scan results disclose the two photon absorption process in the hybrid nanocomposites with self focussing behaviour. With Ag doping, the nonlinearity is found to be increased up to 0.2% Ag doping concentration due to the confined effect of Surface Plasmon, Quantum confinement and thermal lensing. Above 0.2% Ag concentration, its value decreases due to the declined linear refractive index of the nanocomposites. Maximum two photon figure of merit is 76 for 0.2% Ag doped CdSe-PMMA hybrid nanocomposite. The present results accentuate the possibility of tuning the optical non-linearity of CdSe-PMMA hybrid nanocomposite by adjusting the doping concentration.

1. Introduction

In recent years, nonlinear optics have emerged as a promising research field with important applications in various fields such as optical switching, optics communication, high density data storage devices and optical limiting devices [1,2]. The nonlinear optical responses comprise of two different mechanisms: nonlinear refraction and nonlinear absorption. The nonlinear absorption can be further classified into two types (i) saturable absorption (SA), and (ii) reverse saturable absorption (RSA). Nonlinear refraction includes the third- and higher-order nonlinear refractions as well as cascaded second-order nonlinear refraction [3]. Recent investigations have proven that the semiconductor polymer nanocomposites (PNCs) represent a realistic choice for nonlinear optical applications [4,5]. The selection of appropriate synthesis technique for PNCs is an important step for their technological application. The processing chemistry of PNCs is greatly related to the interaction between the polymer and the semiconductor nanoparticles (NPs). The major obstacle during their synthesis is the aggregation of NPs which leads to the quantum confinement effect extinction. The surfactants or ligands are generally used to prevent the aggregation of NPs [6]. In addition to this, the surfactants influence the nanoparticle (NP) behaviour and distribution in the polymer matrix.

Among II–VI semiconductors, cadmium selenide (CdSe) is a direct band-gap semiconductor with bulk band-gap value 1.74 eV and found applications in various fields [7]. Polymer system used in the present study is Poly(methylmethacrylate) (PMMA). It is a transparent polymer and often used in glazing applications as an alternative to glass. It has drawn fabulous interest in optoelectronic devices due to its optical properties. In addition to its excellent optical properties, it has excellent insulating properties, good flexibility, high strength and light weight [8]. To the best of our knowledge, no literature is available on the nonlinear optical properties of CdSe-PMMA hybrid nanocomposites. Gan et al. [9] have studied the nonlinear optical properties of the CdSe/CR39 hybrid composite using single beam Z-scan technique at 794 nm and 397 nm. Liu et al. [10] have studied the high order nonlinear optical properties of CdSe/MOETMA-TFSI composite using a 532 nm picosecond laser. As reported in literature, the addition of Silver (Ag) dopant leads to drastic changes in the physical and chemical properties of the materials [11]. Ag doping also alters the sign of the nonlinear refractive index (n_2) as shown by Kosa et al. [12] in As-S system.

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A lot of literature is available on the synthesis of CdSe-PMMA PNCs and the different researchers had utilized different techniques for its synthesis. Khanna et al. [13] have reported the synthesis of CdSe-PMMA PNC by organometallic chemistry using cadmium metal salt and 1,2,3-selenadiazole as a cadmium and selenium source. However, the whole synthesis process has been performed under nitrogen atmosphere. They have also reported the in-situ synthesis of CdSe-PMMA PNC using cadmium acetate and sodium selenosulphite as a precursors, showing good optical properties [14]. Ingrosso et al. [15] have reported that the interaction between the specific polymer and nanomaterials provides a surface passivation of the nanomaterials resulting in characteristic properties. Recently, the CdSe PNCs with PVA and PVP polymers, synthesized by in-situ technique have been reported by our group [16,17]. To avoid the complications involved in organic synthesis technique, ex-situ technique has been preferred in the present work. N,N-dimethylformamide (DMF) has been used as an organic solvent due to the solubility of PMMA in DMF. Santos et al. [18] have reported that the DMF acts as an active reducing agent for various processes under suitable conditions. They demonstrated that DMF is a powerful reducing agent for silver ions also. This is also the one reason for choosing DMF as a solvent for PNC synthesis.

Here, this article reports the synthesis of Ag:CdSe-PMMA hybrid PNCs at three different Ag concentrations. The structural and morphological study has been carried out to investigate the crystal structure and shape of the nanoparticles. Important linear and nonlinear optical parameters of the PNCs have been extracted from Z-scan technique and semi-empirical relations, respectively.

2. Experimental details

2.1. Chemical materials

Cadmium acetate ($Cd(CH_3COO)_2$) was purchased from Qualigens fine chemicals. Sodium sulphite (Na_2SO_4) and selenium powder were obtained from Loba Chemie Pvt. Ltd. Trisodium citrate (TSC) was purchased from Rankem Pvt. Ltd. PMMA was purchased from Sigma Aldrich. Cetrimonium bromide ($C_{19}H_{42}NBr$), CTAB was purchased from Hi-media Pvt. Ltd. DMF as an organic solvent was purchased from Merck specialities Pvt. Ltd. All of the other chemicals were of analytical grade and were used as purchased.

2.2. Synthesis

CdSe-PMMA nanocomposite was prepared using ex-situ technique. Firstly, CdSe NPs were prepared chemically by using sodium selenosulfate (Na_2SeSO_3) and $Cd(CH_3COO)_2$ as a selenium and cadmium source, respectively.

2.2.1. Preparation of 0.50 M Na_2SeSO_3

0.50 M Na_2SeSO_3 aqueous solution was prepared by adding 0.987 g of selenium powder and 3.15 g of Na_2SO_3 into 50 ml of deionized water under continuous magnetic stirring. The solution was stirred at 60 °C for 7 h. The transparent Na_2SeSO_3 solution was obtained when all the selenium powder was dissolved completely. The solution was cooled and kept under dark conditions to settle down the unreacted selenium if any. The resultant solution was filtered and stored in dark for further use.

2.2.2. Preparation of TSC capped CdSe NPs

0.50 M $Cd(CH_3COO)_2$ solution was prepared in deionized water separately. 0.136 M Trisodium citrate (TSC) was added to cadmium source resulting in milky turbid solution due to the formation of $Cd(OH)_2$ precipitates. The pH of the solution was kept around 10 by using ammonia solution. To above solution, Se source was added dropwise under vigorous stirring at room temperature with Cd:Se precursor ratio 1:1. The colour of solution changes to light yellow, indicating the synthesis of CdSe NPs. The resulting NPs were centrifuged and dried under vacuum conditions for further use.

2.2.3. Aqueous to organic phase transfer

The prepared CdSe NPs are negatively charged due to the citrate ions absorbed on their surface which stabilize the CdSe NPs through electrostatic interaction. To make the CdSe NPs soluble in PMMA matrix solution, the phase transfer technique has been utilized, in which the negatively charged CdSe NPs capped with TSC have been made compatible with the PMMA matrix using CTAB, a cationic surfactant. CTAB makes the surface of CdSe NPs hydrophobic through physical adsorption [19]. CdSe NPs were added to CTAB solution under continuous stirring resulting in precipitation of CdSe NPs indicating the aqueous to organic phase transformation.

2.2.4. Preparation of CdSe-PMMA nanocomposite

The dried CTAB capped CdSe NPs were dispersed in DMF solution and then to PMMA solution (prepared separately in DMF solution at 40 °C under continuous stirring for 2 h) with CdSe NPs to PMMA weight ratio 1:1. The resulting solution was sonicated for 3 h for proper dispersion of CdSe NPs into the polymer matrix. The systematic illustration for the synthesis of CdSe-PMMA nanocomposite is shown in Fig. 1.

2.2.5. Preparation of Ag:CdSe-PMMA hybrid nanocomposite

Ag(x):CdSe-PMMA nanocomposites have been prepared with three different Ag compositions, with x = 0.1%, 0.2% and 0.3% (volume fraction). In brief, 0.3 M $AgNO_3$ solution was prepared in DMF solution. For the preparation of Ag(x):CdSe-PMMA nanocomposites, 10 ml of CdSe PNC solution was put in three different conical flasks. 10, 20 and 30 μl of $AgNO_3$ solution were added to each flask under continuous stirring and the samples were stirred for 2 h. The colour of the solution was observed to change from light orange to brownish orange with the addition of Ag^+ ions to the CdSe PNCs. Thin films of the nanocomposites were prepared on glass substrate using solution casting method for structural and optical characterizations.

2.3. Instrumentation

Crystal structure of the hybrid PNCs was characterized by using a Phillips PW-1710 X-ray diffractometer using CuKα radiation in the 2θ range from 10° to 70°. Transmission Electron Microscopy (TEM) images were recorded using Hitachi H7500 electron microscope with an operating voltage 100 kV and magnification ~1,00,000×. Fourier Transform Infra-Red (FTIR) spectrum was recorded using PerkinElmer PE-RX 1 FTIR spectrophotometer. The spectral resolution of the IR spectrophotometer is ±1 cm^{-1}. Linear optical properties of the samples were studied by recording the transmission spectrum using UV/Vis/NIR computer-controlled spectrophotometer (PerkinElmer LAMBDA 750) in the wavelength range of 400–1200 nm at room temperature. Third order nonlinear optical parameters of the hybrid nanocomposites were studied by Z-scan technique. A continuous wave 2 mW He—Ne Laser operating at a wavelength of 632.8 nm was utilized for these measurements.