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Optical Limiting Characteristics of Core-Shell Nanoparticles

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***Abstract*—**TiO_2 nanoparticles were synthesized by hydrothermal method at 180˚C from $TiOSO_4$ aqueous solution with1m/l concentration. The obtained products were coated with silica by means of a seeded polymerization technique for a coating time of 1440 minutes to obtain well defined $TiO_2@SiO_2$ core-shell structure. The uncoated and coated nanoparticles were characterized by using X-Ray diffraction technique (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) to study their physico-chemical properties. Evidence from XRD and FTIR results show that SiO2 is homogenously coated on the surface of titania particles. FTIR spectra show that there exists an interaction between TiO_2 and SiO_2 and results in the formation of Ti-O-Si chemical bonds at the interface of TiO_2 particles and SiO_2 coating layer. The non linear optical limiting properties of TiO2 and $TiO_2@SiO_2$ nanoparticles dispersed in ethylene glycol were studied at 532nm using 5ns Nd:YAG laser pulses. Three-photon absorption is responsible for optical limiting characteristics in these nanoparticles and it is seen that the optical nonlinearity is enhanced in core-shell structures when compared with single counterparts. This effective three-photon type absorption at this wavelength, is of potential application in fabricating optical limiting devices.

***Keywords*—**hydrothermal method, optical limiting devices seeded polymerization technique, three-photon type absorption

I. INTRODUCTION

THE development of modern optical technology demands the ability to control the intensity of light in a predetermined and predictable manner. In this aspect optical limiters have received significant attention. The search for efficient optical limiters has lead to the study of various materials [1, 2]. Bulk semiconductors [3-5] were first applied to optical limiting because of their diverse optical nonlinearities, such as two-photon absorption (TPA) [4-5], free-carrier non linearities [3] and the Kerr effect [6]. Among the various nonlinear optical materials, direct band gap semiconductors especially TiO_2 and ZnO have attractive non linear properties that make them ideal candidates for NLO based devices. The rapid development of Nanoscience and nanotechnology injects new opportunities into the synthesis of optical materials, as well as the research and design of optical limiters. Nanoscale composite materials containing TiO_2 are interesting because of their potential applications in optoelectronic devices and the bulk TiO_2 has a direct band gap of 3.2eV [7]. A great deal of effort on research has been focused on the synthesis and optical linear properties of TiO_2 nanocomposites. Recently the non linear optical properties of such materials have also received attention. Nanoscale silica nanoparticles have also been extensively studied, due to its CMOS compatibility and enhancement of its non linear effects due to quantum confinement [8]. In the case of silica, the non linearities are usually attributed to two photon related absorption and χ (3) variation related to quantum confinement effects [9-12].

In this paper, we have reported the optical limiting studies on TiO_2 and $TiO_2@SiO_2$ nanoparticles in ethylene glycol using nanosecond laser pulses at 532nm wavelength. The effect of silica coating on the optical limiting is also investigated. It has been observed that Silica coated particles show relatively better optical limiting compared to as prepared TiO_2 nanoparticles.

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II. EXPERIMENTAL

A. Chemicals

Special grade reagents Tetraethylorthosilicate (TEOS) (95%), Titanium Oxysulfate ($TiOSO_4$) were purchased from Sigma Aldrich Chemicals Ltd., Ethanol (99.5%) and ammonia (25% aqueous solution) purchased from (SISCO Research Laboratories, India) were used for silica coating and as catalysts. All other chemicals were reagent grade and used without further purification. Ultrapure deionized water was used in all the preparations.

B. Preparation of titania particles

Anatase-type TiO_2 nanoparticle powder was prepared by the following method. Initially, 18ml of 1m/l of $TiOSO_4$ aqueous solution was taken into a 25ml container of Teflon lined stainless steel autoclave. The container was tightly sealed and was heated at 180°C for 5 hrs with a constant rotation of 1.5 rpm, where hydrolysis of $TiOSO_4$ occurred under autogenous hydrothermal condition. After the completion of the reaction, the precipitate formed was washed several times using double distilled water and decantation. The product was collected at high-speed centrifuge and dried in air at 90°C. The powder thus prepared was heated in an alumina crucible at 700°C in air.

2.3 Silica coating on titania particles

The titania powder thus prepared was coated with silica by means of seeded polymerization technique, using TEOS as a precursor for a coating time of 1440 min at temperatures from 40°C. Titania nanoparticles and ethanol were charged in a 100ml flask and mixed by ultrasonication for 10min to ensure complete dispersion. After sonication predetermined amount of 29wt% aqueous ammonia solution and double distilled water were added. Then a proper amount of TEOS was added to the mixture to carry out the silica growth. The molar ratios of TEOS, ethanol, water and ammonia were 1,100,400 and 20 respectively. After synthesis, the slurry was washed with ethanol twice to remove the secondary silica particles. Finally the prepared sample was annealed to 800°C and characterized.

2.4 Characterizations

FT-IR spectra were recorded on a Perkin Elmer spectrum 2000. X-ray powder diffraction (XRD) measurement was made on (SEIFERT, Germany) with Cukα radiation. TEM image was obtained on a JEOL JEM -3010 Electron microscope, using an accelerating voltage of 300 kV. UV-Vis absorption spectra were obtained using Perkin Elmer Lambda 35 spectrophotometer equipped with an integrating sphere.

III. OPTICAL LIMITING

Optical limiting measurements were carried out at 532nm in solution, using 5 ns laser pulses produced by a Q-switched, frequency-doubled Nd:YAG laser (Minilite, Continuum Inc.). Optical limiting data were extracted from open aperture z-scan experiments. In our experiment we used lens of 20cm focal length. The laser pulses were plane polarized with a Gaussian spatial profile. At each position *z,* the sample sees different laser intensity, and the position dependent (ie, intensity-dependent) transmission is measured using an energy meter placed after the sample. Laser pulses are fired at a repetition rate of 1 Hz, and the data acquisition is automated. The low repetition rate is chosen for avoiding thermal effects in the samples during measurement. The pulse energy reaching the sample is approximately 150 μJ.

IV. RESULTS AND DISCUSSION

4.1 XRD analysis

The XRD pattern of the as prepared TiO_2 annealed at 700°C for 3 hrs and silica coated TiO_2 nanoparticles is shown in the fig (1). After calcination, the TiO_2 powders are identified to have sharpened diffraction peaks can be well indexed to tetragonal structure (lattice cell parameters a=3.777A JCPDS File NO. 89-4921). All the peaks can be assigned to anatase phase and no diffraction peaks due to other impurity phases are detected. The average crystallite size is calculated using the Scherrer equation, estimated from the XRD line broadening was around 16-19nm. For silica coated TiO_2 nanoparticles, peaks for TiO_2 are not clearly seen due to dense silica coating on its surface. The presence of amorphous silica effectively suppresses the sharpened peaks of TiO_2. Moreover, the suppression is more remarkable with the introduction of higher silica content.

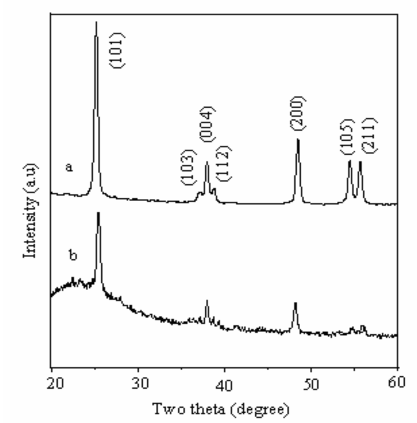


Fig. 1 XRD pattern of TiO_2 and $TiO_2@SiO_2$

4.2 FT-IR Spectrum

Fig (2) shows the FT-IR spectra of pure TiO_2 and Silica coated TiO_2 nanoparticles. The peaks at 1099 cm^{-1}, 800 cm^{-}1 and 470 cm^{-}1 correspond to the asymmetric, symmetric and anamorphic streches of Si-O-Si. The absorption peak at 3457 cm^{-1} is attributed to the O-H stretching vibration of free water and its corresponding O-H bending vibration occurs at 1636 cm^{-1} due to the chemically adsorbed water [13]. The IR band observed at 951 cm^{-1} indicates the existence of Ti-O-Si chemical bonding as the IR bands observed from 910 to 960 cm^{-1} are widely accepted as the characteristic vibration due to the formation of Ti-O-Si bond [14].

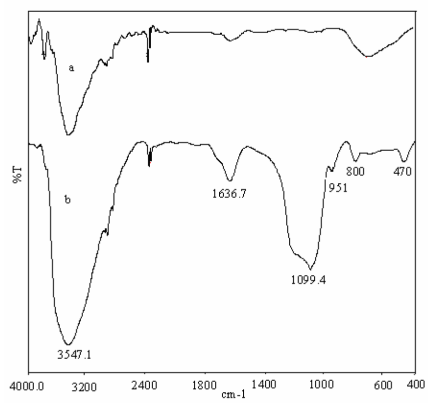


Fig. 2 FT-IR spectra of pure TiO_2 and Silica coated TiO_2

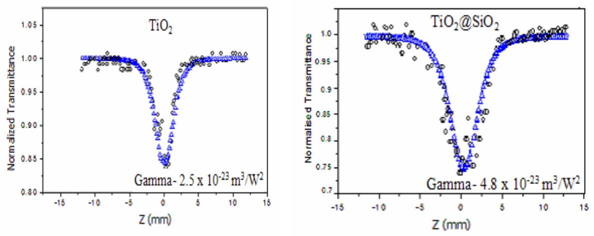
4.4 Optical Limiting Studies

Open-aperture z-scan measurement on the samples was performed with the intention of calculating their nonlinear absorption coefficients. Interestingly, the nonlinear transmission is found to arise from three-photon type absorption.

The experimental data fits well to the corresponding nonlinear transmission equation, given by

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi}\, p_0} \int_{-\infty}^{+\infty} \ln\left[\sqrt{1 + {p_0}^2 \exp(-2t^2)} + p_0 \exp(-t^2)\right] dt$$

where 'R' is the surface reflectivity and p_0 is given by $2\gamma(1-R)^2 I_0^2 L$, where γ is the three photon absorption co-efficient and I_0 is the on-axis peak intensity. α is the linear absorption coefficient. The z-scan signatures for TiO_2 and Silica coated TiO_2 are shown in Figures 3 (a) and (b) respectively.



(a) (b)

Fig. 3. Open aperture Z-Scan traces of TiO_2 and Silica coated TiO_2 nanoparticles.

The non linear absorption coefficient is higher in the core-shell nanoparticles as compared to uncoated nanoparticles, in confirmation with a previous report [15]. The three photon absorption data fitted well with the experimental curves, indicating that three-photon absorption is the basic mechanism of optical limiting.

V. CONCLUSIONS

Titania nanoparticles were synthesized and coated with amorphous silica by a seeded polymerization technique. Evidence from XRD and FTIR results show that SiO_2 is homogenously coated on the surface of titania particles. The average particle size of TiO_2@SiO_2 nanoparticles was roughly found out to be about 24nm. FTIR spectra show that there exists an interaction between TiO_2 and SiO_2 and results in the formation of Ti-O-Si chemical bonds at the interface of TiO_2 particles and SiO_2 coating layer. Nonlinear optical transmission measurements at 532 nm using 5 ns laser pulses on the TiO_2 as well as TiO_2@SiO_2 core-shell nanoparticles show the existence of an effective three-photon type absorption at this wavelength, which may be of potential application in fabricating optical limiting devices.

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