Tailoring optical properties of TiO_2 in silica glass for limiting applications*

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We present the linear and nonlinear optical studies on TiO_2–SiO_2 nanocomposites with varying compositions. Optical band gap of the material is found to vary with the amount of SiO_2 in the composite. The phenomenon of two-photon absorption (TPA) in TiO_2/SiO_2 nanocomposites has been studied using open aperture Z-scan technique. The nanocomposites show better nonlinear optical properties than pure TiO_2, which can be attributed to the surface states and weak dielectric confinement of TiO_2 nanoparticles by SiO_2 matrix. The nanocomposites are thermally treated and similar studies are performed. The anatase form of TiO_2 in the nanocomposites shows superior properties relative to the amorphous and rutile counterpart. The involved mechanism is explained by rendering the dominant role played by the excitons in the TiO_2 nanoparticles.

Keywords: reverse saturable absorption (RSA), optical limiting, excitons

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1. Introduction

The need for efficient nonlinear optical materials is motivated by widespread areas of applications, such as all-optical switches, optical memory, spectroscopy, imaging, ultrashort pulse generation, entangled photon generation, and quantum cryptography.[1] Generally, the nonlinear optical effects are prominent in high optical intensity regime due to the weak nonlinear optical response exhibited by most of natural materials. As a result, materials possessing large third-order nonlinearity and fast temporal optical response are highly demanding. Materials with negligible linear absorption and hence possessing better transparency are potential candidates in developing practical nonlinear optical devices. TiO_2 has been in the scientific limelight because of their irreplaceable role in applications related to environmental cleaning and protection, photo catalysis, gas sensing, fabrication of solar cells and batteries. In addition, TiO_2 possesses high refractive index and fast, as well as reasonably large, nonlinear optical response.[2] In this report, we present the studies on the optical properties of TiO_2/SiO_2 nanocomposites. Quantum-sized semiconductors doped in glass matrix has been found to be very promising. The electronic properties of these materials change drastically due to the dielectric confinement created by the glass matrix which in turn improves their nonlinear optical properties. It is evident from our study that such kind of dielectric confinement leads to remodelling of the electronic band structure which in turn is closely linked to the electronic trap states present either on the crystal surface or in the glass matrix. The presence of excited electrons in these states permanently modifies the absorption and the electronic de-excitation routes.[3] Here, we present the study on the modification in the optical properties of TiO_2 caused by incorporating it in SiO_2 matrix. We study their nonlinear optical absorption in the off-resonance region by Z-scan technique. The obtained results are discussed in terms of cumulative effects due to the enhancement in the dielectric confinement with the amount of SiO_2.

2. Experiment

Here we report the synthesis and characterization of TiO_2–SiO_2 nanocomposites. The synthesis is completed by simple sol gel process. Tetraethylorthosilicate (TEOS) ($Si(OC_2H_5)_4$) and titanium tetrabutoxide (TTBO) ($Ti(OC_4H_9)_4$) were used as precursors for SiO_2 and TiO_2, respectively. TEOS and TTBO were dissolved in absolute ethanol separately to form two pre-solutions. TEOS was first mixed with absolute ethanol with a molar ratio of 1:4, hydrolysed by adding 0.1 N HCl to adjust the water to alkoxy molar ratio to 2:1, and then stirred with a magnetic stirrer at room temperature. For pure TiO_2, TTBO was hydrolysed in absolute ethanol by adding a few drops of concentrated HNO_3 and then stirred for 30 min. The two solutions were mixed with various TEOS/TTBO molar ratios and stirred for 1 h.[4] Subsequent amorphous powders were obtained from the prepared solutions. The obtained powders were heated at 500 °C and 900 °C respectively to obtain the anatase and rutile crystalline counterparts of TiO_2. In this report, 25T–75S composite refers to 25%TiO_2–75%SiO_2 in the composite. The nanocomposites are characterized by optical absorption measurements recorded by using a UV/VIS/IR spectrophotometer

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(JascoV-570). In the present investigation, we employed the single-beam Z-scan technique with nanosecond laser pulses (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) to measure the nonlinear absorptive and refractive properties of nanocomposites. Z-scan technique developed by Bahae *et al.* is a single-beam method for measuring the sign and magnitude of nonlinear refractive index n_2 and has sensitivity comparable to interferometry methods.[5] The sample is moved in the direction of light incidence near the focal spot of the lens with focal length of 20 cm. The Rayleigh length z_0 is estimated to be 7.4 mm, much greater than the thickness of the sample cuvette (1 mm), which is an essential criterion for Z-scan experiments. The data are analyzed by using the procedure described by Bahae *et al.*, and the nonlinear coefficients are obtained by fitting the experimental Z-scan plot with the theoretical curves.

3. Results and discussion

Optical absorption measurement is an initial step to observe the nanocomposite behaviour. Figure 1(a) plots the room-temperature absorption spectra of the nanocomposites. The absorption edge of TiO_2 is found to be blue shifted with respect to their bulk, which could be attributed to the quantum confinement effects. The optical band gap can be estimated by plotting $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$ based on the relation

$$\alpha h\upsilon = A(h\upsilon - Eg)^{1/2}, \tag{1}$$

where α is the absorption coefficient, A is a constant, and E_g is the band gap. According to the above relation, the intercept of the tangent on the photon energy axis corresponds to optical band gap.[6]

All samples have high transmittance in the visible region. Furthermore, higher SiO_2 content results in higher transparency in the visible region, due to the smaller particle size and higher dispersity. In Fig. 1(b), the optical band gaps E_g for 100T, 25T–75S, 50T–50S, and 75T–25S are found to be 3.85, 3.93, 3.89, and 3.86 eV, respectively. Here it is found that as the SiO_2 amount in the nanocomposites increases, the band gap also increases. This signifies the diminishing size effect on TiO_2 in the SiO_2 matrix. Figures 1(c) and 1(d) present the variation in the absorption and band gap of 25T–75S after annealing at 500 °C and 900 °C, respectively. They show that annealing induces the growth of TiO_2 particles dispersed in the glass matrix. The fact that increasing SiO_2 content resulted from a decreasing particle size has been confirmed by the XRD analysis taken after annealing the samples at 500 °C and 900 °C by using the Debye–Scherrer equation (see Fig. 2).

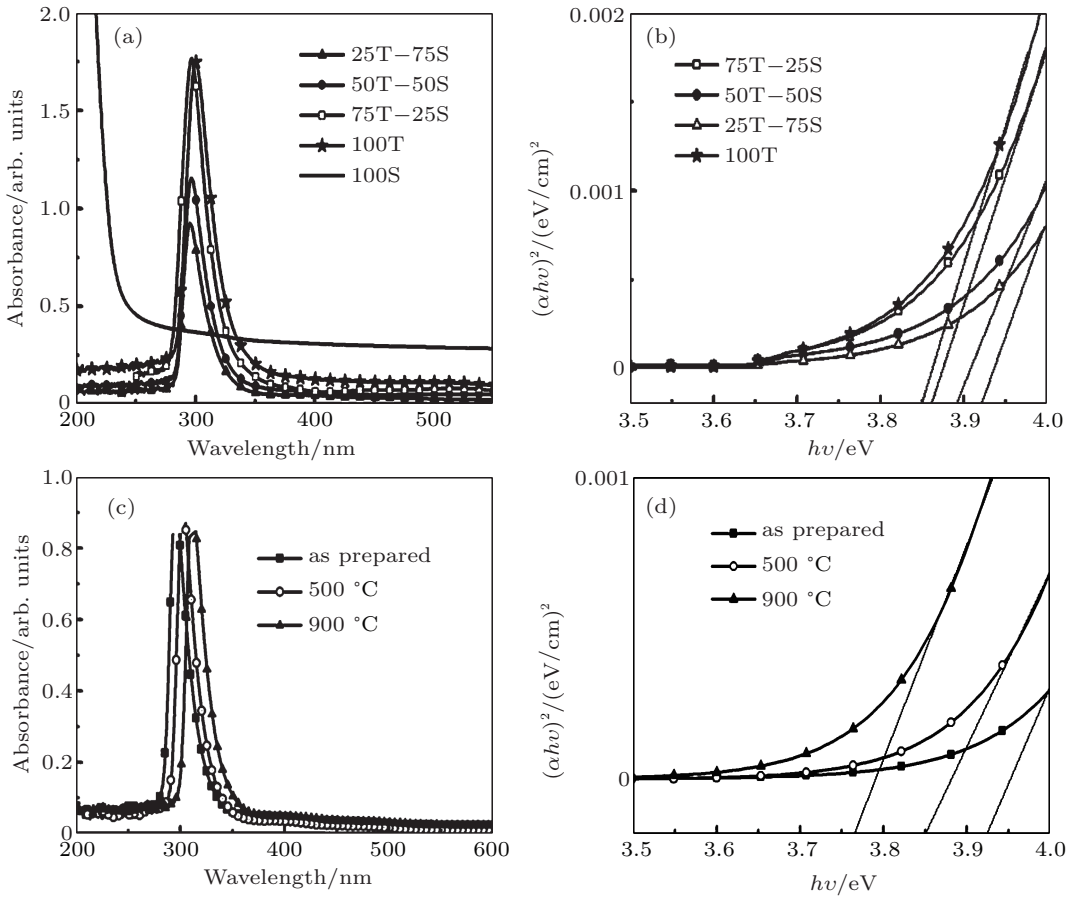


Fig. 1. (a) Absorption spectra of the nanoparticles. (b) Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for determining the band gap of the nanoparticles. (c) Aabsorption spectra of the 25T–75S annealed at different temperatures. (d) Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for determining the band gap of the nanoparticles.

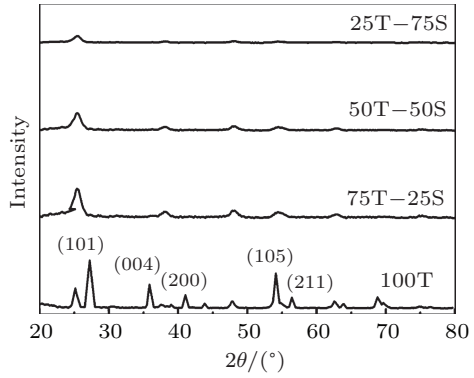


Fig. 2. XRD patterns of composites prepared with various Ti:Si ratio after annealing at 500 °C.

The pores in mesoporous SiO_2 matrix are highly dispersive and allow the probable flow of TiO_2 sol between adjacent pores. During gel progress, movement of TiO_2 is hindered due to the surface tension of the solution. This probably makes the TiO_2 particles in our sample less aggregated and well dispersed. Thus, with increasing annealing temperature, the TiO_2 particles dispersed in the films become bigger, and hence TiO_2 has higher mobility.[7] The band gap varies as per the size of the nanoparticle. Figure 3 represents the FTIR spectra of the 25T–75S nanocomposites. Similar results are obtained for all the nanocomposites. The peaks at 1082.69 cm^{-1}, 961.15 cm^{-1}, and 469 cm^{-1} are anamorphic stretches of Si–O–Si. The absorption peak at 3463.68 cm^{-1} is due to the O–H stretching vibration of free water and its corresponding O–H bending vibration at 1640.94 cm^{-1} due to the chemically adsorbed water.[8] The IR band observed at 961 cm^{-1} indicates the existence of Ti–O–Si chemical bonding as the IR bands observed from around 910 cm^{-1} to around 960 cm^{-1} are widely accepted as the characteristic vibration due to the formation of Ti–O–Si bond.[9] Thus, from FTIR spectra, it can be confirmed that Ti–Si nanocomposites have been formed.

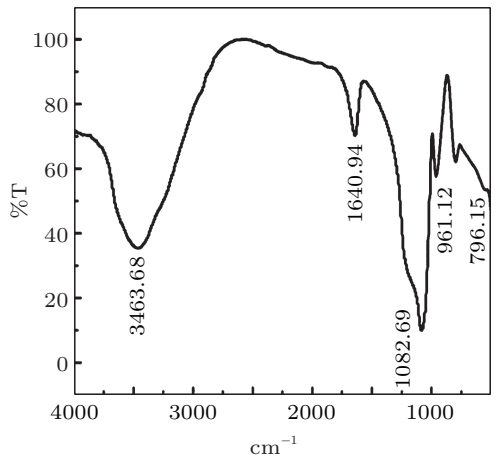


Fig. 3. FTIR spectra of the 25T–75S nanocomposites.

The technique of open-aperture Z-scan scheme is employed to study the nonlinear optical properties of the system. In order to ensure that no permanent photo-induced change to the sample occurs during laser irradiation, we repeat the experiment by illuminating the sample at the same position. The normalized transmittance for the open-aperture condition is given by

$$T(z) = \frac{C}{q_0\sqrt{\pi}} \int_{-x}^{x} \ln(1 + q_0 \mathrm{e}^{-t^2})\,\mathrm{d}t, \tag{2}$$

where

$$q_0(z,r,t) = \beta I_0(t) L_{\mathrm{eff}}, \quad L_{\mathrm{eff}} = 1 - \mathrm{e}^{-\alpha l}/\alpha, \tag{3}$$

and L_{eff} is the effective thickness of the film with linear absorption coefficient α, and I_0 is the irradiance at focus. Under the experimental conditions, laser beam illumination at 532 nm usually gave rise to reverse saturable absorption (RSA) curve due to two-photon absorption (TPA) process as the photon energy of 532-nm laser is within the range $E_g < 2h\nu < 2E_g$, where $h\nu = 2.33$ eV. TPA occurs when TiO_2 nanoparticles absorb the energy of two photons to get excited to the higher energy state. The Z-scan traces are made for all different compositions with four different input power densities. The Z-scan traces obtained at 464.8 MW/cm^2 are shown in Fig. 4. The fitting of Eq. (1) to the experimental data are depicted in this figure by the solid curves.

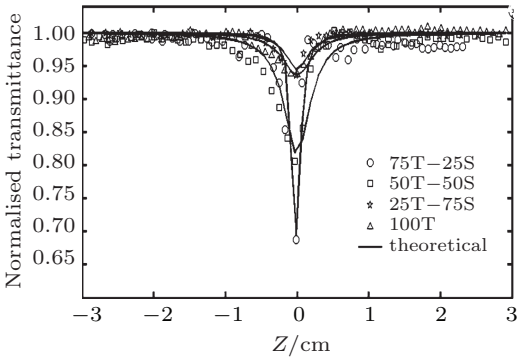


Fig. 4. Normalized transmittance as a function of the position in the open aperture scheme at 532 nm with a laser power of 464.8 MW/cm^2.

Figure 5 represents the dispersion of nonlinear absorption coefficient β as a function of the parameter $x = h\upsilon/E_g$, where $h\upsilon$ is the incident photon energy. This form of presentation facilitates the discussion on the physical origin of the nonlinearity. From the Z-scan results, it is obvious that the nonlinear optical properties of nanohybrid thin films show strong dependence on the titanium oxide loading. The nonlinear absorption coefficient β is found to increase linearly with the percentage of TiO_2 and shows large enhancement in contrast to pure titania. Such large enhancement can be due to the fact that TiO_2 nanoparticles possess distinct surface structure and high surface activity, so that their optical properties will

change with surrounding environment. When TiO_2 nanoparticles with large interface are embedded in SiO_2 matrix having smaller dielectric coefficient, there will be a strong charge interaction between them consequently, resulting in an electric dipole layer at the nanoparticle surface. This effect also depends on the permittivity ratio between particles and surrounding medium. This surface polarization commonly known as dielectric confinement effect further accelerates the separation of excited charges, and thus finally enhances the electric field inside the nanoparticles.[10] Moreover, it can change the charge density distribution of nanoparticle surface, which further strengthens the anharmonic vibration of surface electron. Enhanced Raman scattering is produced at the interface due to the different permittivity, so the light intensity inside particles is different from that of surrounding medium, and hence it gives rise to local-field effect which is responsible for the enhanced nonlinear response.[11] Another contributing factor to the enhancement of nonlinearity can be imperfect surface modification of titania nanoparticles. There are many physically trapped states or chemical dangling bonds within or on the surface of the nanoparticles. Hence, surface states are easily formed due to a large number of defects at the surface of TiO_2 nanoparticles which eventually makes an important contribution towards the enhanced nonlinearity of nanocomposites. The decay time of surface states are long enough to induce several trapped electrons, which are transferred to higher surface states.

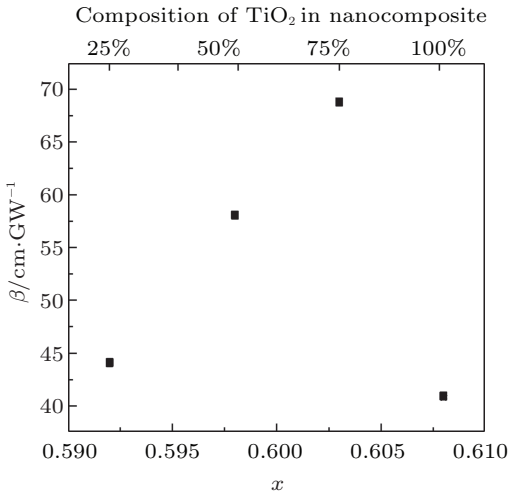


Fig. 5. Dispersion of nonlinear absorption coefficient (β) of nanocomposites as a function of the parameter $x = h\upsilon/E_g$, where $h\upsilon$ is the incident photon energy and percentage of TiO_2 in the composition.

Figure 6 represents the plot of TPA coefficient β versus $h\upsilon/E_g$ for different crystalline forms of TiO_2, anatase and rutile form of 25T–75S formed at 500 °C and 900 °C, respectively. It is observed that β increases with annealing temperature. This can be attributed to the fact that with increase in the annealing temperature, size of TiO_2 increases. The resultant enhancement of nonlinear optical properties with increasing dimension in the weak confinement regime originates from the size-dependent enhancement of oscillator strength of coherently generated excitons.[12] The confinement of excitonic wave function is expected to give rise to enhancement of the oscillator strength by a factor of R^3/a_B^3, where R is the particle size and a_B is exciton effective Bohr radius. To be of special concern, anatase film annealed at 500 °C shows better nonlinear absorption than the rutile counterpart. This is attributed to the fact that anatase is characterised by presence of more imperfections and disorder. This favours impurity diffusion and disorder creation in anatase crystals.[13] Additionally, anatase phase has self-trapped excitons, whereas the rutile phase has free excitons. Nonlinear optical effects are usually enhanced when the associated optical transition has large optical oscillator strength, and hence anatase has larger TPA coefficient than the rutile phase.[14]

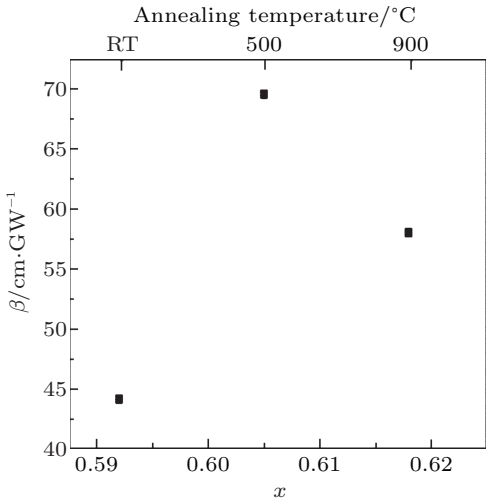


Fig. 6. Dispersion of nonlinear absorption coefficient (β) of 25T–75S nanocomposite as a function of the parameter $x = h\upsilon/E_g$, where $h\upsilon$ is the incident photon energy.

Recently, a commendable amount of research has been devoted to the field of optical limiting applications. Usually the materials used are organic matter or semiconductors, mainly in liquid state which are restrained in the aspects of stability and limiting performance. It has been observed that inorganic material has stable physicochemical property as well as high damage threshold. Hence, it becomes significant to study the role of the nanocomposites for optical limiting applications. Figure 7 represents the optical limiting performance of our nanocomposites. The optical limiting threshold is the corresponding fluence value at which the deviation from linearity in the normalized transmittance is observed. The limiting graph indicates that our nanocomposites show better performance than pure titania.

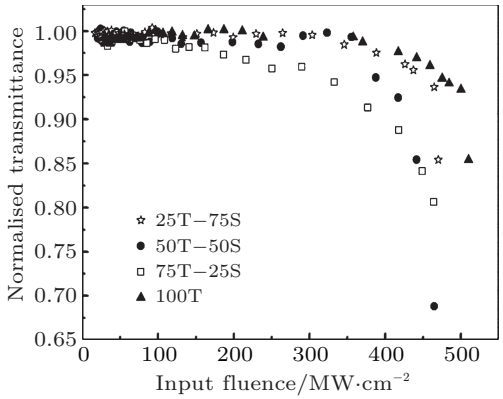


Fig. 7. Optical limiting response of nanoparticles at 532 nm and an input power density of 464.8 MW/cm^2. The optical limiting threshold is found to decrease with increasing percentage of TiO_2 in the composition.

4. Conclusion

In conclusion, TiO_2–SiO_2 semiconductor-doped glass system of various composition has been synthesised. Linear and nonlinear optical properties have been studied using optical absorption, and open aperture Z-scan technique. Structural characterizations are performed using XRD and FTIR. Optical limiting characteristics are studied and their potential candidature for optical limiting applications is confirmed.

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