Electronic and optical properties of TiO_2 and its polymorphs by Z-scan method*

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TiO_2 is a material which has attracted considerable attention from the scientific community for its innumerable properties. TiO_2 is known to exist in nature in three different crystalline structures: rutile, anatase, and brookite. Anatase and rutile TiO_2 films have been widely characterized for their potential applications in solar cells, self-cleaning coatings, and photocatalysis. In the present report, the third-order nonlinear susceptibilities of TiO_2 and its polymorphs, anatase, and rutile, prepared by the sol–gel technique followed by heat treatment are investigated using the Z-scan technique at a wavelength of 532 nm with a duration of 7 ns. Imaginary and real values of $\chi^{(3)}$ for amorphous, anatase, and rutile are also calculated and found to be 5×10^{-19} m^2/V^2, 27×10^{-19} m^2/V^2, 19×10^{-19} m^2/V^2, respectively. It is found that the values of the optical constants of amorphous TiO_2 after heat treatment vary considerably. It is assumed that this could be due to the variation in the electronic structure of TiO_2 synchronous with the formation of its polymorphs, anatase, and rutile. Amorphous TiO_2 is marked by the localization of the tail states near the band gap, whereas its crystalline counterparts are characterized by completely delocalized tail states.

Keywords: excitons, reverse saturable absorption (RSA), excitonic nonlinearity

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1. Introduction

Titaniumdioxide (TiO_2) belongs to a fascinating class of inorganic solids, which has been investigated for many years. It has attracted much attention over the last decades for its desirable properties such as non-toxicity and good stability in various environmental conditions. In addition to being frequently used in technological applications such as photovoltic solar cells and photocatalysis with promising efficiency, it also proves its suitable candidature in areas such as the production of paints, paper, plastics, cosmetics, etc.[1–3] TiO_2 is a high band gap semiconductor transparent to visible light and has exceptional optical transmittance. It possesses a high refractive index and good insulating properties. Besides its various applications, due to its low cost and safety towards humans and our environment, it can be considered beneficial to humankind in all respects. Crystalline TiO_2 exists in three different forms, i.e., anatase, rutile, and brookite, depending on the fabrication method and heat treatment. Among these three, rutile is the most thermodynamically stable phase, anatase and brookite are metastable phase and are transformed to rutile on heat treatment. Qualities such as higher values of refractive index, dielectric constant, electric resistance, and stability favour the rutile phase more than anatase.[4] Usually brookite exists as an impurity in anatase and rutile phases, and hence these two remain the most investigated forms. In this paper, we mainly focus on the electronic and optical properties of amorphous, anatase, and rutile phases. Studies related to their electronic and optical properties using an orthogonalised linear-combination-of-atomic-orbitals method have already been reported.[5] However, here we expound the variation in the properties of these two forms by considering the role played by excitons through analyzing their nonlinear phenomenon studied using the Z-scan technique. The opposite natures of exciton states in anatase and rutile correlate with their structural differences. Anatase is characterised by self-trapped ones whereas rutile is characterised by free excitonic states.[6] Here TiO_2 nanoparticles are synthesized by the sol–gel method and are transferred to their crystalline phases by heat treatment. The characteristics of the nanoparticles are analyzed from the results of an open and closed aperture Z-scan experiment using a nanosecond laser (7 ns). By performing Z-scan experiments, the real and imaginary parts of the third-order nonlinear susceptibility are determined. The nonlinearity of nanoparticles in such cases is attributed to excitonic absorption due to the photo-excited generation of excitons. From these studies, it can be confirmed that TiO_2 belongs to the class of direct band gap semiconductors exhibiting very large optical nonlinearity due to an excitonic effect. These kinds of materials are widely acclaimed for their potential applications in the field of all-optical signal processing. Here we try to explain the physics of bound excitons and the giant non-linearities associated with them. The short radiative lifetime associated with this large oscillator strength allows fast switching in a nonlinear optical device operated at near-resonant wavelengths.

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2. Experiment

The TiO_2 sol was prepared by the sol–gel method and synthesized as follows. Titanium tetra-butoxide (TTBO) was used as the precursor to prepare TiO_2 sol. A mixture of HCl and butyl alcohol was added to a mixture of TTBP and butyl alcohol under continuous magnetic agitation at room temperature. The TiO_2 sol composition was of molar ratio TTBP/butanol/water = 1 : 26.5 : 1.5. The [H+]/[TTBO] molar ratio ranged from 0.02 to 1.1. The resulting TiO_2 sol was clear and stable. The as-obtained nanoparticles were thermally treated at 100 °C to remove the excess moisture content. Thus amorphous TiO_2 nanoparticles were obtained. Further, these amorphous nanoparticles in powder form were subjected to 500 °C and 900 °C to obtain the anatase and rutile TiO_2 respectively.

The prepared TiO_2 samples were characterised by optical absorption measurements using a (JascoV-570) UV/VIS/IR spectrophotometer. The values of the nonlinear absorption coefficient (ß) and nonlinear refractive index of the samples were calculated using an open aperture and closed aperture Z-scan technique by employing a Nd-YAG laser (532 nm, 7 ns, 10 Hz). The Z-scan technique developed by Bahae *et al.* is a single beam method of measuring the sign and magnitude of nonlinear refractive index n_2 and has sensitivity comparable to interferometry methods.[7] The sample was moved in the direction of light incidence near the focal spot of the lens with a focal length of 200 mm. The Rayleigh length z_0 was estimated to be 7.4 mm, which is much greater than the thickness of the sample cuvette (1 mm), an important criterion for Z-scan experiments. The data were analyzed by using the procedure described by Bahae *et al.*, and the nonlinear coefficients were obtained by fitting the experimental Z-scan plot to the theoretical plots.

3. Results and discussion

Figure 1 represents the band gap variations of the different phases of TiO_2 with temperature. The optical band gap is obtained by plotting $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$ based on the relation

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

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 the optical band gap. The band gap of the semiconductor decreases with increasing the annealing temperature. This could be due to the fact that when the samples are subjected to a higher temperature, the crystallites begin to move and start agglomerating. Hence the band gap decreases with increasing size.

Figure 2 represents the XRD patterns of amorphous, neither anatase nor rutile TiO_2. Amorphous TiO2 has any characteristic crystalline peak. The experimental spacings are compared with those reported for rutile (110) (2θ of 27.45°) and anatase (101) (25.24°) to identify the particle structure.[8]

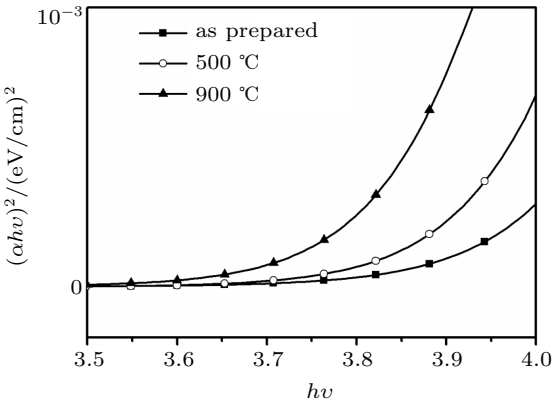


Fig. 1. Determination of the band gap of amorphous TiO_2 and its polymorphs anatase and rutile obtained by heating amorphous TiO_2 at 500 °C and 900 °C respectively.

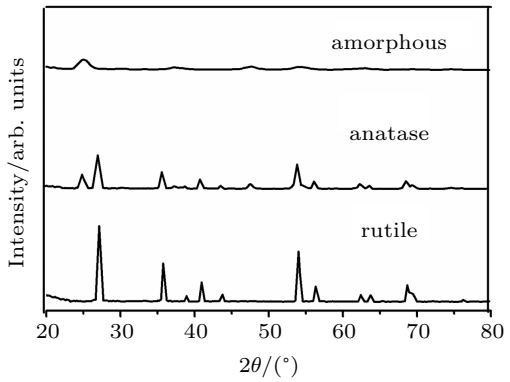


Fig. 2. XRD patterns of the obtained nanoparticles.

The third-order nonlinear optical properties of nano TiO_2 samples are investigated using the Z-scan technique and are represented in Figs. 3 and 4 at a laser power of 196 MW/cm^2. In order to ensure that no permanent photo-induced change occurs to the sample 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[7]

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

where $q_0(z,r,t) = \beta I_0(t) L_{\mathrm{eff}}$, with

$$L_{\mathrm{eff}} = 1 - \mathrm{e}^{-\alpha l}/\alpha, \tag{3}$$

in which L_{eff} being the effective thickness of the film with linear absorption coefficient α and I the irradiance at focus. Linear absorption coefficients of the samples were: 0.0238, 0.0113, 0.0252 for amorphous, anatase, and rutile respectively. The obtained curves follow the reverse saturable absorption (RSA) nature. Under the experimental conditions, the laser

beam illumination at 532 nm usually corresponds to the two-photon absorption (TPA) process, because the photon energy of the 532-nm laser is within the range $E_g < 2h\nu < 2E_g$, where $h\nu = 2.33$ eV. Z-scan traces are made for all the different phases at different input power densities. The Z-scan traces are shown in Fig. 2, where the fitings of Eq. (1) to the experimental data are depicted in the figure by the solid curves. The induced absorptions in the samples are indicated by the transmittance valleys. Figure 4 represents the closed aperture Z-scan traces of the samples. The closed aperture curve exhibits a peak to valley shape, indicating a negative value of the nonlinear refractive index n_2. It is observed that the peak–valley of the closed aperture Z-scan satisfies $\Delta z \sim 1.7z_0$, thus confirming the presence of cubic nonlinearity.

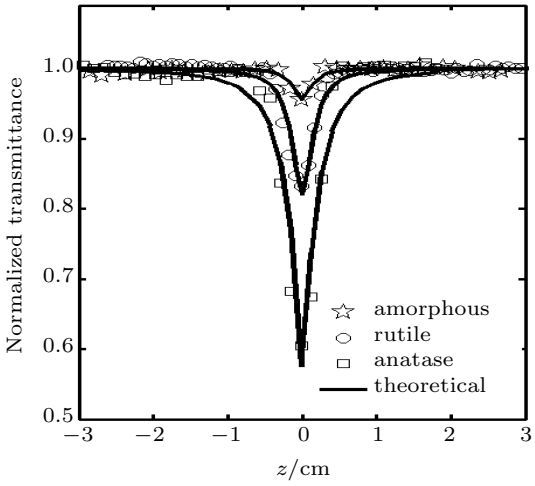


Fig. 3. Variations of calculated and measured normalized transmittance with the position in the open aperture scheme at 532 nm with a laser power of 196 MW/cm ^{2}.

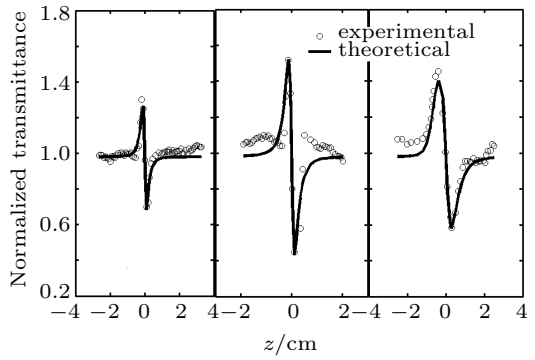


Fig. 4. Variations of normalized transmittance with the position in the closed aperture scheme at 532 nm at a laser power of 196 MW/cm^2.

In the case of a closed aperture,

$$T(z,\Delta\varphi_0) = 1 + \frac{4\Delta\varphi_0 x}{(x^2+9)(x^2+1)}, \tag{4}$$

where $x = z/z_0$ and $\Delta\varphi_0 = 2\pi n_2 I_0 L_{\text{eff}}/\lambda$.

Here, from Figs. 3 and 4 it is evident that as the annealing temperature increases, the nonlinearity increases. This can be attributed to the fact that with the increase of annealing temperature, the size of TiO_2 increaes and this corresponds to the enhancement of the nonlinear optical properties with increasing dimension in the weak confinement regime, originating from the size-dependent enhancement of oscillator strength of coherently generated excitons.[9] Excitons are electronic excitations of semiconductors and insulators comprising electron–hole pairs linked through Coulomb correlated force, as represented in Fig. 5. Exciton polaritons are composite quasi-particles formed by the coupling of light and dipole-active excitons.[10]

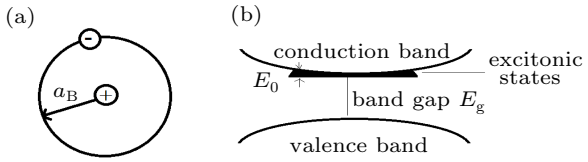


Fig. 5. (a) Model for the electron–hole pair for exciton states. (b) Location of the exciton states relative to the conduction and valence bands.

Sometimes the generation of excitons leads to ionic relaxation, which eventually traps the excitons within a single lattice constant thus localizing it and hence known as bound excitons. Bound and free excitons are pictorially represented in Fig. 6. The confinement of excitonic wave function is expected to give rise to the enhancement of the oscillator strength by a factor of R^3/a_B^3, where R is the particle size and a_B is the exciton effective Bohr radius. But as expected, the rutile phase does not have a larger nonlinearity than the anatase phase. This may be due to the fact that anatase has bound excitons and hence a larger excitonic binding energy, whereas the rutile phase is characterized by free excitons with negligible binding energy. In both polymorphs, the excitonic wave functions are two-dimensional and this planar distribution is localized in just one atomic layer in the anatase case. This stronger localization probably supports the possibility of experimentally reported self-trapping.[11] Usually the nonlinear optical effect is enhanced when the associated optical transition has large optical oscillator strength. As reported by Rashba and Gurgenishivili, excitons weakly bounded to impurities have giant oscillator strengths that are many orders of magnitude larger than the oscillator strength per molecule of the free exciton.[12] An exciton weakly bounded to a center can be considered as a quasi-particle moving in the field of the center as a single entity; the radius of this state exceeds that of the internal motion in the excitons and hence it possesses a weaker oscillator strength and consequently, a lower magnitude of nonlinearity.

In order to confirm the role of thermal nonlinearity, we perform a thermal lens experiment.[13] The excitation source used is a continuous wave (cw), 532-nm diode pumped solid state (DPSS) laser. The DPSS laser has a maximum power of 150 mW. A 2-mW He–Ne used as the probe is arranged to

be collinear with the pump laser, using a dichroic beam splitter. Figure 7 shows the experimental thermal lens development curve and theoretical curve fitting for amorphous TiO_2.

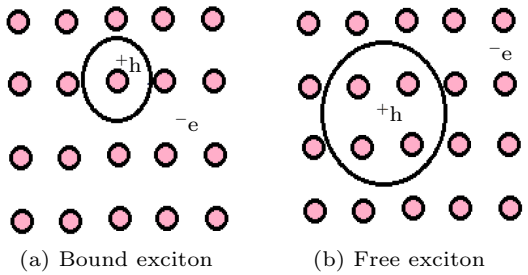


Fig. 6. (color online) (a) Bound excitons: the electron is strongly bounded and confined within a single lattice constant. (b) Free excitons: the electron is weakly bounded within an average radius larger than the lattice constant.

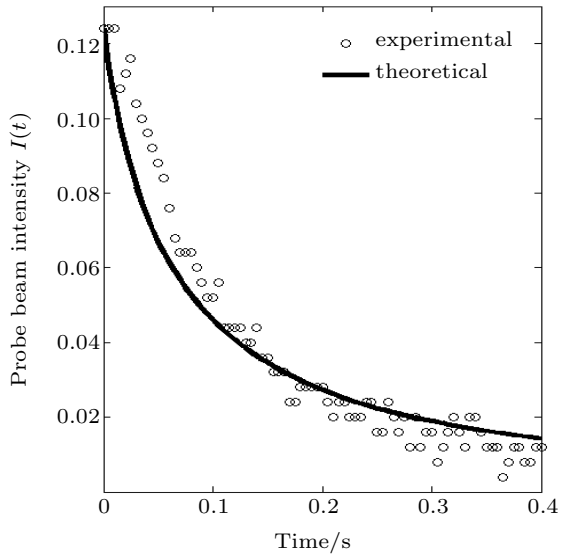


Fig. 7. Decay curve for amorphous TiO_2 nanoparticles.

The characteristic thermal-diffusion time, t_c, is a critical parameter that determines the magnitude of the thermal effect. If the sample is illuminated by a train of pulses whose spacing is smaller than the thermal characteristic time $t_c = w^2/4D$ (where w is the laser spot size, and D is the thermal diffusion coefficient of the matrix), thermal diffusion effects come into play. Here, the pulse width $\tau_p = 7$ ns is much smaller than the build-up time of the thermally induced optical nonlinearities, which are 1.02 s, 1.67 s, 1.12 s for the amorphous, anatase, and rutile phases respectively. Hence the thermally induced optical nonlinearity plays a crucial role in determining the nonlinear characteristics of the sample.

From the relations reported by Sheikh Bahae *et al.*, the optical constants are determined.[7,14–16] The values for nonlinear susceptibility of amorphous, anatase, and rutile phases are determined to be 5×10^{-19} m^2/V^2, 27×10^{-19} m^2/V^2, 19×10^{-19} m^2/V^2, respectively.

Figure 8 illustrates the optical limiting responses of samples at an input laser intensity of 196 MW/cm^2. The optical limiting threshold is seen to decrease with the increase of temperature and hence particle size. But as expected, the rutile phase does not have a lower threshold than the anatase phase, which may be due to its reduced nonlinearity. The optical limiting threshold is the corresponding fluence value at which the deviation from linearity in the normalized transmittance is observed. It is obvious that the lower the optical limiting threshold, the better the optical limiting material is. The annealing temperature and hence the particle size has a significant effect on the optical limiting performance of a TiO_2 sample.

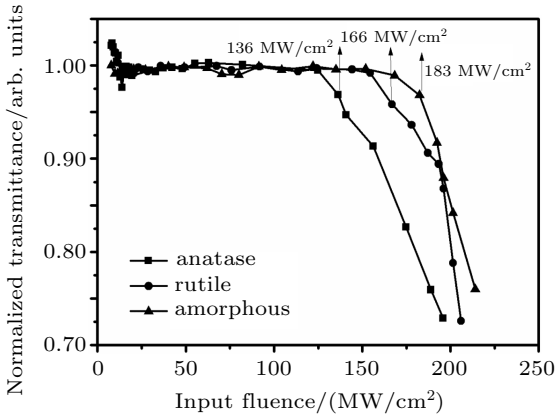


Fig. 8. Optical limiting responses of various forms of TiO_2. Anatase is found to have a limiting ability superior to amorphous and rutile TiO_2.

4. Conclusion

In this paper, we demonstarate the nonlinear optical properties of TiO_2 and its two important polymorphs, anastase and rutile. The nonlinear optical response of the nanoparticles is studied using a nanosecond laser. Studies reveal an RSA nature, which is explained through two-photon absorption followed by the dominant role played by excitons. The optical limiting thresholds are calculated for all three phases, and the results reveal that the anatase phase shows the better limiting capability than the amorphous and rutile phase of TiO_2. The values for the nonlinear susceptibility of amorphous, anatase, and rutile phases are found to be 5×10^{-19} m^2/V^2, 27×10^{-19} m^2/V^2, 19×10^{-19} m^2/V^2, respectively.

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