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Spectral and nonlinear optical transmission studies of Zr^{4+}-doped TiO_2 nanoparticles

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ABSTRACT

Zr^{4+}-doped TiO_2 nanoparticles with a homogeneous anatase structure were synthesized through sol–gel technique. The crystalline phase and particle sizes of the resultant particles were investigated by X-ray diffraction (XRD), Raman and transmission electron microscopy (TEM) techniques. Results indicated that Zr^{4+} was incorporated into the lattice and interstices of titania nanocrystals. The amount of Zr^{4+} doping decreased the size of particle, and enhanced "blue-shift" in the UV–vis absorption spectra. The optical limiting property of the samples was assessed by a *Z*-scan technique in which the Zr^{4+}/TiO_2 nanoparticles dispersed in ethylene glycol were excited at 532 nm using 7 ns Nd:YAG laser pulses. Experimental results indicated that at 0.5 and 1.0 mol% doping of Zr^{4+} the particles exhibit three-photon absorption while for at 2.0 and 3.0 mol% dopant concentration the data fitted to saturable absorption followed by two-photon absorption.

1. Introduction

The search for materials with large nonlinear optical properties for the development of communication networks such as optical switches, optical power limiters, optical detectors and optical sensors have grown rapidly because of their applications for scientific and industrial purposes [1,2]. The successful fabrication and use of these devices depends upon the availability of good nonlinear optical materials. Various materials such as inorganics, organics, organometallics and semiconductors have been studied for their nonlinear optical properties [3–5]. Recently, interest in the designing of optical limiting devices has surged due to the advent of nanoparticles and nanostructures. In this perspective, Semiconductor nanoparticles have proven to be the best candidate for their excellent linear and nonlinear optical properties. Of the various semiconductor materials studied, titanium (IV) oxide (TiO_2) found to be a suitable material for these applications as it exhibits quite interesting properties and is also transparent over a large spectral range. By carefully selecting the appropriate matrix element, one can easily tune the physical properties and recognize various applications. The synthesis of transparent semiconductor with appropriate dopant is nowadays of great interest because it can be tailored chemically by varying the size, shape and composition to fit wide range of applications in nonlinear optics. As a result, several investigations have been carried out the study of the NLO properties of TiO_2 composites [6–8].

Different process like nonlinear scattering two-photon or three-photon absorption, transient absorption, interband absorption and reverse saturable absorption phenomena including free carrier and excited state absorption responsible for optical limiting are reported to be operative in these nanostructures. However, some reports have revealed that under the similar excitation of laser pulses many materials possess more than one nonlinear absorption process simultaneously. The possibility of the simultaneous occurrence of different mechanisms in the same material giving rise to strong optical limiting properties cannot be ruled out. Therefore, it is of great importance to distinguish the nonlinear absorption effects and to determine the nonlinear absorption parameters for the materials exhibiting more than one nonlinear absorption effect. The most widely used techniques to characterize nonlinear absorption are based on nonlinear transmittance measurements introduced by Sheik-Bahae et al., also known as *Z*-scan technique. This technique has been extensively used as an effective and convenient tool for determining the nonlinear absorption properties of various materials [9–13]. Furthermore, the *Z*-scan method is not restricted to the investigation of fluorescent materials. These aspects have made *Z*-scan the most used technique for measuring nonlinear absorption processes.

Here we present the investigation of nonlinear optical properties of Zr^{4+}-doped TiO_2 nanoparticles prepared via the sol–gel process. At 0.5 and 1.0 mol% dopant concentration of Zr^{4+}, the nonlinearity is mainly due to three-photon absorption while at 0.2 and 0.3 mol% dopant concentration of Zr^{4+}, absorption saturation behaviour followed by two-photon absorption (2PA) coexists.

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2. Experimental

2.1. Synthesis

Zr^{4+} doped TiO_2 nanoparticles with different volume ratio of Zr^{4+} (0.5, 1.0, 2.0 and 3.0 mol%) prepared by sol–gel method [14] is as follows. Initially, 18.6 ml of titanium (IV) isopropoxide was hydrolyzed by 35.8 ml glacial acetic acid at 0 °C. To this solution, zirconium (IV) oxynitrate dissolved in 395 ml of water was added drop wise under vigorous stirring for 1 h and the stirring was continued for further 5 h. The prepared solution was kept in dark for 24 h for nucleation process. After the period, the solution was placed in an oven at 70 °C for 12 h for gelation and ageing process. The gel was then dried at 100 °C and subsequently the product was crushed into fine powder.

During the sol–gel synthesis of Zr^{4+}-doped TiO_2 nanoparticles, high water ratio was kept to enhance the nucleophilic attack of water on titanium (IV) isopropoxide and to suppress the fast condensation of titanium (IV) isopropoxide species to yield TiO_2 nanocrystals.

2.2. Characterizations

The XRD patterns were recorded on a PANAalytical X'pert PRO X-ray diffractometer using Cu Kα radiation as the X-ray source. UV–vis absorption spectra were obtained on a Perkin Elmer Lambda 35 spectrophotometer. The fluorescence and its lifetime measurements was done on a fluorolog system (Horiba Jobin Yvon), equipped with a choice of nanoLEDs emitting-1 ns pulses at 280 nm. TEM images were obtained on a JEOL JEM-3010 Electron microscope, using an accelerating voltage of 300 kV.

2.3. NLO properties measurements

Optical limiting properties were investigated from open aperture *Z*-scan experiments with 7 ns laser pulses at 532 nm from a frequency doubled, Q switched Nd:YAG laser (Minilite Continuum Inc.). The standard experimental setup of *Z*-scan measurement is shown in Fig. 1. Samples were prepared by dispersing the nanoparticles in ethylene glycol and the solution was taken in a 1 mm cuvette. The samples were adjusted to have the linear transmittance of 65%. The spatial profile of the pulsed beam was of nearly Gaussian form after spatial filtering. The pulsed beam was split into two parts: the reflected part was used as reference, and the transmitted part was focused onto samples by using a 20-cm focal length lens. The beam's propagation direction is taken as the *Z*-axis, and the focal point is taken as $Z = 0$. On approaching the focus the intensity increases by several orders of magnitude relative to the intensity away from focus, inducing nonlinear absorption in the sample. Laser pulses were fired at a repetition rate of 1 Hz, and the data acquisition was automated. The pulse energy reaching the sample was approximately 150 μJ.

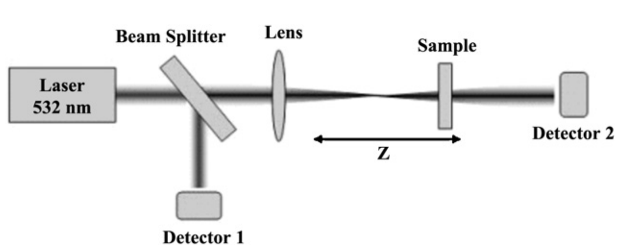

Fig. 1. Schematic of the open aperture *Z*-scan setup.

3. Results and discussions

3.1. UV–vis spectra

In order to explore the optical response of the obtained Zr^{4+}-doped TiO_2 nanoparticles, the diffused reflectance spectroscopy (DRS) were measured at room temperature are shown in Fig. 2. The absorption spectrum of TiO_2 at 400 nm is due to the charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t_2g orbitals of the Ti^{4+} cations) [15]. The spectra reveal that Zr^{4+} doping in TiO_2 nanoparticles shifts the absorption edge towards higher wavelength, that is, towards the visible region with a substantially long band tailing. A step increase in the absorption at ~400 nm can be assigned to the intrinsic absorption band gap of TiO_2. It is proposed that the enhanced ability for visible light absorption may partly ascribe to the formation of intermediate energy levels or surface trap states. Moreover, the intensity of this absorption bands was found to increase with increasing in ZrO_2 content.

3.2. Steady-state fluorescence spectra

For nanostructured materials, the fluorescence spectra are related to the transfer behaviour of the photoinduced electrons and holes so that it can reflect the separation and recombination of photoinduced charge carriers. Employing an ultraviolet light with a 280 nm wavelength as the excitation source, the fluorescence emission spectra of Zr^{4+}-doped TiO_2 nanoparticles with different concentration of Zr^{4+} are recorded as shown in Fig. 3. The spectra demonstrate that Zr^{4+} content on TiO_2 has an impact to the relative intensity of fluorescence spectra. The emission peak at 390 nm is attributed to the direct transition from the conduction band to the valence band [16]. The intensity of the spectrum decreases with increase in Zr^{4+} concentration. The decrease in the emission intensity may due to introduction of new defect sites such as oxide ion vacancy [17]. Since, the peak intensity depends upon the defects concentration which clearly depicts that on increasing the doping concentration defects levels increases thus inhibiting recombination of electron-hole pairs makes the intensity decrease. The lower PL intensity of the Zr^{4+}-doped sample clearly implies lower recombination rate.

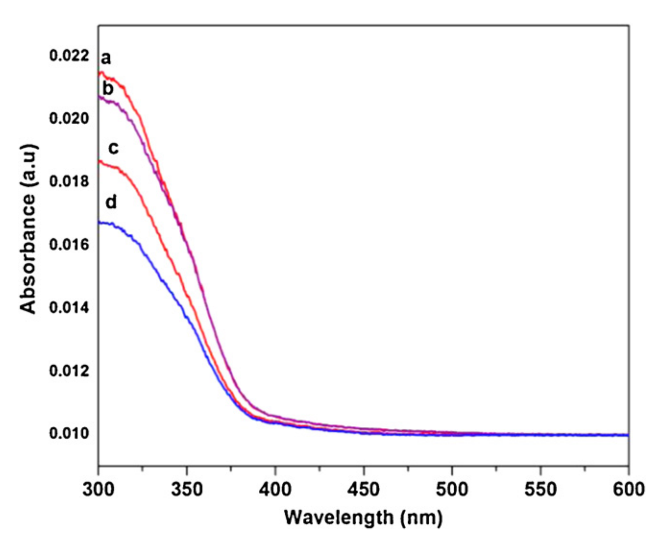

Fig. 2. UV-DRS spectra of Zr^{4+} doped TiO_2 nanoparticles: (a) 0.5, (b) 1.0, (c) 2.0, and (d) 3.0 mol% Zr^{4+}.