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Review Article

Micro-structural, linear and nonlinear optical properties of titania nanoparticles

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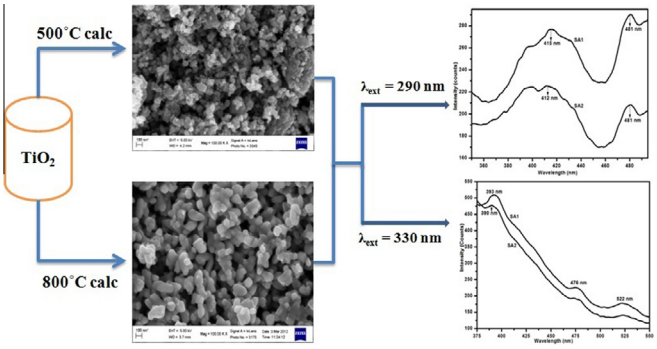
HIGHLIGHTS

- Micro-structural parameters of titania nanoparticles were calculated.
- Young's modulus was determined more precisely for each ($h\,k\,l$) planes.
- The band edge emission was observed with different excitation phenomena.
- Second harmonic generation was observed for centrosymmetric nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO_2 (titania) nanoparticles were prepared by sol–gel method using titanium tetrachloride as precursor and calcined at 500 °C (SA1) and 800 °C (SA2). X-ray diffraction pattern of SA1 has mixed phases of anatase (17%) and rutile (83%) whereas SA2 has pure rutile (100%) TiO_2. From the X-ray diffraction peak profile analysis, the crystallite size, lattice strain, deformation stress and energy density value of TiO_2 nanoparticles were determined more precisely by Williamson–Hall method, uniform deformation model, uniform stress deformation model, uniform deformation energy density model and size–strain plot method. The calculated average crystallite size from uniform stress deformation model is 21 and 53 nm for SA1 and SA2 respectively. From the FTIR spectra Ti–O vibrational frequency is observed at ~530 cm^{-1}. Using Tauc's relation the direct bandgap of SA1 and SA2 is calculated from UV–vis spectra as 2.75 and 2.95 eV respectively. The excitation wavelength dependent photoluminescence has been investigated for 290 and 330 nm as excitation wavelengths. It was observed that the band edge emission is decreased with respect to excitation wavelengths. The second harmonic generation efficiency (SHG) observed for centrosymmetric rutile TiO_2 is more comparable with KDP crystal.

Contents

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Introduction

Nanocrystalline TiO_2 is one of the fascinating semiconducting materials due to the unique properties and several technological applications in photo catalysis, solar cells and gas sensing [1–3]. TiO_2 has three crystalline polymorphs: anatase, rutile and brookite. Anatase and brookite are in meta stable phase but can be transformed into rutile on heating. For photocatalytic and solar cell applications, anatase phase is more preferable. However, rutile has some advantages over anatase such as higher dielectric constant, refractive index, electric resistance and good chemical stability. Due to these properties, rutile titania nanoparticles are used in capacitors, optical filters and power circuits. The particle size, crystallinity and morphology of TiO_2 nanoparticles affect the performance of these devices. According to the kinematical scattering, X-ray diffraction peaks has broaden either when crystallite becomes smaller than about a micrometer or of lattice defects are present in abundance. W–H analysis is a simplified integral breadth method where size-induced and strain induced peak broadening is deconvoluted by considering the peak width as a function of 2θ. Crystal imperfections, such as lattice dislocations, crystallite size and lattice strain increase the peak width and shift the 2θ peak position accordingly [4,5]. Luminescence measurement yields information about the energetic positions of the electronic states in the bandgap. Such localized state can be due to various types of imperfections like vacancies, interstitial atoms and grain boundaries [6,7]. Bulk TiO_2 does not show any photoluminescence at room temperature, but nano TiO_2 exhibit many luminescence peaks in the visible region, due to the presence of self trapped excitons, surface trap states, interstitial Ti^{3+}, oxygen defects etc. [8,9]. The study of nonlinear optical properties such as the second harmonic generation efficiency (SHG) is of particular interest in photonic crystals (PCs), because of their unique dispersion properties and potential applications in novel optical devices.SHG is strongly sensitive to the symmetry of the system. Nanoparticles have large surface to volume ratio. The surface of nanoparticles plays a crucial role in determining their linear and nonlinear optical properties. SHG is forbidden in the bulk of a centrosymmetric medium, while at the surface, inversion symmetry is broken and thus SHG is observed [10–12]. So the surface sensitivity of the SHG is observed for the centrosymmetric rutile titania nanoparticles.

In this paper, the effect of stress and strain is estimated by W–H analysis, uniform deformation model (UDM) and the modified form of W–H analysis namely uniform stress deformation model (USDM), uniform deformation energy density model (UDEDM) and size strain plot (SSP). Defect related phenomena by fluorescence spectrum are also investigated. The powder SHG efficiency of titania nanoparticles has been measured.

Experimental details

All the chemicals were of analytical grade. 4.5 mL of $TiCl_4$ was slowly added dropwise into 45 mL of ethanol at room temperature. A large amount of HCl gas was exhausted during the mixing process. A light yellow solution was obtained and gelatinized for 120 h. The sol–gel solution was vaporized at 80 °C until a dry gel was obtained. This as-synthesized compound was calcined at 500 °C for 1 h (sample SA1) and 800 °C for 1 h (sample SA2).

The crystalline structure of the synthesized nanopowder was analyzed by X-ray diffraction, using a PANalytical Xpert PRO diffractometer with the wavelength of 1.5406 Å (Cu Kα). FTIR spectrum was taken using a JASCO-460 PLUS FTIR spectrometer by KBr pellet technique. Shimadzu 1800 UV–vis spectrometer was used to examine the absorption spectrum of synthesized nanoparticles. Morphology was analyzed using FESEM (Carl Zeiss). Room temperature fluorescence spectrum was recorded using Fluoromax spectra fluorometer with Xenon lamp as the excitation source. The second harmonic generation efficiency (SHG) of titania nanoparticles was measured by Kurtz & Perry powder technique. In this technique, the sample was sandwiched between two glass slides and subjected to the output of a Q-switched Nd:YAG laser (1064 nm, 10 Hz and 9 ns). SHG is confirmed by the green emission at 532 nm.

Results and discussion

X-ray diffraction

Fig. 1 shows the XRD pattern of TiO_2 at calcining temperatures (500 and 800 °C). The samples were indexed with JCPDS No. (21-1276) for rutile and JCPDS (21-1272) for anatase phases. It confirms that the TiO_2 nanoparticles have tetragonal crystal structure. The sample calcined at 500 °C exhibit peaks of both the anatase and rutile phases [13]. The weight fraction of rutile phase was calculated based on the following equation:

$$W_R = \frac{I_R}{K_A I_A + I_R} \qquad (K_A = 0.886) \tag{1}$$

where W_R is the weight fraction of rutile and I_A and I_R are intensity of anatase and rutile from the peak areas of anatase (1 0 1) and rutile (1 1 0) diffraction planes respectively. Substituting the values of I_A and I_R in Eq. (1), the weight fraction of rutile for 500 °C calcined sample is estimated as 83%. Mixed phase (anatase–rutile) of TiO_2