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Oxygen defect dependent variation of band gap, Urbach energy and luminescence property of anatase, anatase–rutile mixed phase and of rutile phases of TiO_2 nanoparticles

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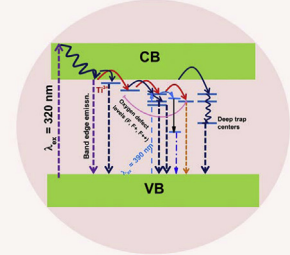
HIGHLIGHTS

- Vacuum annealed TiO_2 has small band gap and high Urbach energy.
- The Urbach energy is higher in mixed phase TiO_2 than that in pure anatase or rutile phase.
- The visible emission peaks are due to excitons and charged oxygen defects.
- Oxygen vacancies are responsible for the long lifetime of the carriers.

GRAPHICAL ABSTRACT

Ti^{3+} forms shallow trap centers and oxygen vacancies form both shallow and deep trap centers. These defects reduce the band gap and increases carrier concentration.



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ABSTRACT

TiO_2 nanoparticles are prepared by a sol–gel method and annealed both in air and vacuum at different temperatures to obtain anatase, anatase–rutile mixed phase and rutile TiO_2 nanoparticles. The phase conversion from anatase to anatase–rutile mixed phase and to rutile phase takes place via interface nucleation between adjoint anatase nanocrystallites and annealing temperature and defects take the initiate in this phase transformation. The samples are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis and photoluminescence spectroscopy (PL). Anatase TiO_2 exhibits a defect related absorption hump in the visible region, which is otherwise absent in the air annealed samples. The Urbach energy is very high in the vacuum annealed and in the anatase–rutile mixed phase TiO_2. Vacuum annealed anatase TiO_2 has the lowest emission intensity, whereas an intense emission is seen in its air annealed counterpart. The oxygen vacancies in the vacuum annealed samples act as non-radiative recombination centers and quench the emission intensity. Oxygen deficient anatase TiO_2 has the longest carrier lifetime. Time resolved spectroscopy measurement shows that the oxygen vacancies act as efficient trap centers of electrons and reduce the recombination time of the charge carriers.

1. Introduction

TiO_2 has wide range of applications in photocatalysis, solar cells, fuel cells, chemical sensors, electrochromic displays, planar waveguides, etc. [1–5]. One of the important areas of application of TiO_2 is in photocatalysis but because of the wide band gap its application is limited up to ultraviolet (UV) light only. For visible light photocatalysis the band gap of TiO_2 should be narrowed and the carrier separation should be increased. Doping is one way by which the band gap of TiO_2 can be narrowed and the carriers can be separated, but in many cases the dopant acts as the recombination center and decreases the numbers of free available carriers

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[6,7]. Therefore, dopant free reduced or defective TiO_2 is gaining immense attention for all of the aforementioned applications because of the formation of localized defect states that traps the photoexcited electrons and reduces the band gap of TiO_2 [8,9]. Naldoni et al. [8] synthesized a reduced TiO_2 having a band gap of 1.85 eV. Chen et al. [9] prepared black colored TiO_2 nanoparticles with band gap of 1.0 eV. Tao et al. [10] prepared dopant free defective TiO_2 with band gap of 2.1 eV. Recent study reported that anatase–rutile mixed phase and rutile phase of TiO_2 also exhibit photocatalytic activity [11,12]. Cha et al. [11] reported that the photoactivity of rutile TiO_2 is enhanced by dislocations produced in the band gap of TiO_2. They reported photoluminescence (PL) peaks in the range between 2.1 and 2.8 eV and attributed these emissions to the dislocations present in the band gap. On the other hand, Su et al. [12] reported that a mixture of 60% anatase and 40% rutile mixed phase TiO_2 exhibit better photoactivity than individual anatase or rutile polymorphs. Baiju et al. [13] with the help of photoluminescence (PL) spectroscopy reported that anatase–rutile mixed phase has reduced PL intensity and longer carrier lifetime, whereas a short lifetime is reported when rutile content increases. Oxygen deficient TiO_2 thin film is reported to exhibit two important absorption peaks at 2.5 eV and 3.0 eV, assigned to surface and bulk oxygen vacancies respectively [14]. In all these samples the reduced band gap is attributed to oxygen defects [8–10,14]. Steady state and time resolved photoluminescence (PL) spectroscopy are the two most essential tools to identify structural defects in a material and these techniques provide information on the radiative or non-radiative recombination in a material [13,15–18]. These two tools along with UV–vis spectroscopy can examine the defect induced variation in the band gap, defect present in the material, charge carrier recombination, etc.

In this article we have reported the optical properties of defective anatase, anatase–rutile mixed phase and of rutile phase of TiO_2 nanoparticles. TiO_2 has immense applications in photocatalysis but to be an efficient photocatalytic material it should have absorption in the visible region as well as large number of available free carriers. We have prepared defective TiO_2 and observed that oxygen defects are mostly responsible for the reduction in band gap and for the separation of carriers. Apart from the defective anatase, anatase rutile mixed phase has reduced band gap because of the presence of interface defects and due to the different alignment of the band states in anatase and rutile. The band gap of rutile is large and the carriers have short lifetime because of the removal of crystalline defects. In this work a thorough study is carried out on the relationship of defects with the band gap, Urbach energy, carrier recombination. This study may help in understanding the role of defects on the absorption and photoluminescence property of TiO_2 so that based on these observations the photocatalytic efficiency of TiO_2 can be enhanced.

2. Synthesis details of TiO_2 nanoparticles

2.1. Preparation of anatase, anatase–rutile mixed phase and rutile TiO_2 nanoparticles

TiO_2 nanoparticles were prepared by the sol–gel method. The synthesis was started by pouring 15 ml of 2-propanol into 6 ml of titanium isopropoxide solution. The solution was allowed to stir for 15 min and then 1 ml of water was added to the titanium isopropoxide-2-propanol mixture. Appearance of white turbidity, on addition of water, indicated initiation of the hydrolysis of isopropoxide chain. Stirring was continued for nearly 6 h and during this time period first a white sol was formed which ultimately transformed into a thick gel. The stirring was automatically stopped when the solution became a gel. The gel was left in aging condition for 8–10 h. After this time period the gel was sonicated in ethanol and then centrifuged in water and ethanol 3 times each. The centrifuge tube containing titania was left in a hot air oven at 80 °C for drying. The dried amorphous titania was annealed in vacuum at 200 °C for 3 h. This sample was labeled TV3. This sample was divided into 3 parts and annealed in air at 450 °C, 700 °C and 950 °C. These samples were labeled as TA450, TA700 and TA950 respectively.

2.2. Characterization details

XRD pattern was observed in a Rigaku miniflex X-ray diffractometer equipped with intense Cu Kα radiation (λ=0.154 nm) at a scanning rate of 1°/min. Transmission electron microscope (TEM) images were taken by using JEOL-JEM TEM at an operating voltage of 200 kV. Diffuse reflectance spectra (DRS) were obtained by using a Shimadzu 2450 UV–vis spectrophotometer. Photoluminescence spectra were examined in a Perkin Elmer LS-55 fluorescence spectrometer. Time resolved photoluminescence (TRPL) spectra were obtained with life spec II spectrofluorimeter (Edinburgh instrument). The sample was excited by a laser diode of wavelength 475 nm.

3. Results and discussion

The structural phases of the prepared TiO_2 nanoparticles are studied with X-ray diffraction. Fig. 1 demonstrates the diffraction pattern of TV200, TA450, TA700 and TA950. Most of the diffraction peaks of TV200 and TA450 match with the diffraction peaks of anatase TiO_2 (JCPDS 78-2486), except for the peak at $2\theta \sim 30.5^\circ$. This diffraction peak corresponds to the brookite phase of TiO_2 (JCPDS-761934). TA950 has only the rutile phase (JCPDS-894920). Therefore, TV200 and TA450 contain minor brookite phase, the majority of the peaks being of anatase phase. Kandiel et al. [19] reported that below 600 °C both anatase and brookite phases are predominant and beyond this temperature both the phases slowly

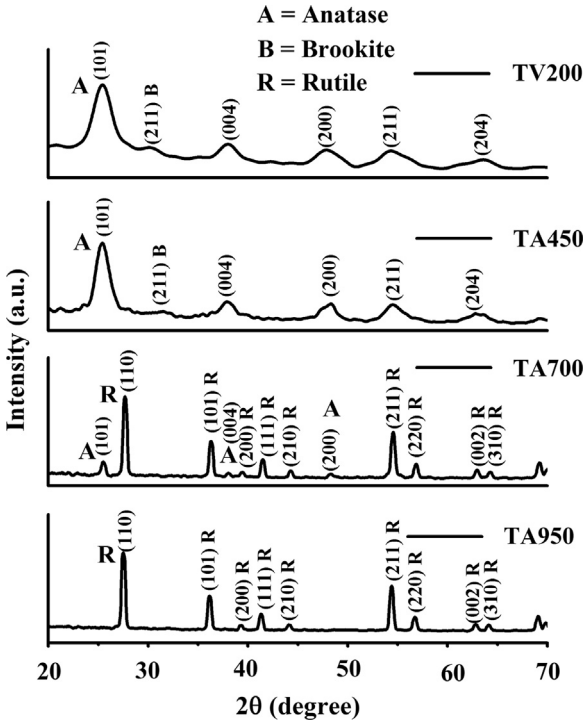

Fig. 1. X-ray diffraction pattern of TV200, TA450, TA700 and TA950.