Research Article

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Structural and Optical Characteristics Transformation in the Sol-Gel Synthesized Pure Titanium Dioxide

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ABSTRACT

The TiO_2 nanocrystals gaining wide spread attention in research in the field of solar cells, biosensors and photo catalysts due to its remarkable optical and electrical properties. In this present work the titanium dioxide nano crystals were synthesized by using titanium isopropoxide as precursor and isopropyl alcohol as solvent. The ratio of the precursor and the solvent were controlled to bring out the sol-gel. The analysis was carried out for as synthesized sample and the sample annealed at 450 °C, reviles the anatase to rutile phase transformation. SEM photograph confirms the transformation due to annealing. The XRD pattern shows both the samples are in nanoscale with average grain size of 7 nm and 17 nm respectively. The EDX shows the prepared samples are titanium dioxide without any impurity. The UV-Vis absorption study shows that the annealing decreases the band gap of TiO_2.

Keywords: Biosensor; So-gel; Solar cell; TiO_2.

1. INTRODUCTION

TiO_2 has been one of the most extensively studied oxides because of its remarkable optical, electrical and optoelectronic properties (Patil *et al.* 2009). Nanoclusters of metals and semiconductors are considered as building blocks of the future modern technologies (Mane *et al.* 2005). Nano-crystalline TiO_2 are currently receiving widespread attention as a low-cost alternative material in conventional inorganic photovoltaic devices (Weiying *et al.* 2005). The band gap of TiO_2 is about 3.2 eV. Its band gap has limited its use for the application of solar cell to electrical energy conversion. However in 1991 Gratzel and co-workers made a breakthrough by preparing low cost, high efficiency dye–sensitized solar cells using nanocrystalline porous TiO_2 thin film, where the light harvesting efficiency was increased to almost 100% because of high surface area of the porous TiO_2 thin film (Mosaddeq-ur-Rahman *et al.* 1997).

The performance of TiO_2 nanomaterial is highly dependent on several parameters, like morphology, crystalline phase, surface area and single crystalline. The physicochemical properties of TiO_2 nanomaterials vary with their size and morphology (Regan *et al.* 1991). The smaller the particles size of TiO_2, the larger the specific surface area. For the TiO_2 particles between 1 and 10 nm in size, the band-gap energy of TiO_2 depends on the particle size due to the quantum size effect: The smaller the particle size, the higher is the band-gap energy of TiO_2. TiO_2 has been extensively used in environmental studies, dye-senstized solar cells (Roberson *et al.* 2004), electro chromic displays (Zhaoyue Liu *et al.* 2005), gas sensors (More *et al.* 2008) and photocatalytic studies (Cao *et al.* 2004). Due to the demand of TiO_2 in different applications, simple and low cost techniques are required for preparation. Many methods are available for the preparation of TiO_2. Sol-gel method is an easiest method of producing pure TiO_2 nanocrystalline (Sanghun Loe *et al.* 2001). The setup is simple and can work at room temperature. In sol-gel method more precise control of particle size and porosity is achieved by adjusting one or more parameters, like sol concentration, washing methods, annealing temperature etc. In the present study sol-gel method has been used for the preparation of TiO_2 using titanium isopropoxide as precursor. In this paper, we report the effect of annealing temperature solution on the properties of the prepared TiO_2 films.

2. EXPERIMENTAL METHOD

The TiO_2 nano powder was prepared by the sol-gel method. Titanium isopropoxide was used as the titania precursor, isoproponal was used as solvent. The matrix sol was prepared by mixing 1.1 mL of TIP with 15 mL of isoproponal at room temperature and stirred for 1 hr. Later titanium isopropoxide is added drop wise and stirred vigorously and obtained a homogeneous mixture

of TiO_2 sol. The sol was in the colour of moonstone yellow. The pH measured was 5.8. The mixed solution was then transferred into a 100 mL Teflon autoclave without stirrer, sealed with a stainless steel lid, and aged at 120 °C for 24 hrs and then aged at an elevated hydrothermal temperature of 150 °C for desired period of 48 hrs for the nucleation and growth of titania particles. The obtained white solid products were centrifuged and washed at 4500 rpm for 5 min. Then the powder was motored and annealed at 450 °C.

Crystalline and phase analysis of the films were carried out by X-ray diffraction method (Rigaku Rint 2000 series). The optical properties were studied using the absorbance spectra of UV-Vis spectroscopy (Jasco V-570). The chemical characterizations of the sample were carried out by EDX. The surface morphology of the samples was studied using scanning electron microscopy.

3. RESULTS & DISCUSSIONS

TiO_2 nanocrystalline have three well-known phases namely anatase, rutile and brookite. Rutile and anatase are tetragonal where as brookite is orthorhombic. Rutile is the only stable phase. Anatase and brookite are metastable at all temperatures and can be converted to rutile after heat treatment at high temperatures (Kun-Mu Lee *et al.* 2007).

The crystal nature and orientation of the TiO_2 nano powder were investigated by X-ray diffraction (XRD) pattern. TiO_2 nano powder have been prepared by sol gel method. The prepared TiO_2 nano powder was analyzed by as prepared and annealed at 450 °C. Fig. 1 shows the X-ray diffraction pattern of TiO_2 powder prepared on sol-gel process as prepared. X-ray diffraction pattern has been used to investigate the phase of the prepared TiO_2 powder. The diffraction peak in the pattern corresponds to (101) (200) and (004) phase of TiO_2 in as prepared sample and the diffraction peak in the pattern corresponds to (110) (211) and (101) phase of TiO_2 in annealed sample. The peak position and their relative intensities are consistent with the standard powder diffraction pattern of anatase TiO_2 (JCPDS card 84-1286) for as prepared sample and rutile TiO_2 (JCPDS card 21-1276) for annealed sample. The crystallite size has been determined using the Scherer's formula (Senthil *et al.* 2014).

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\,\theta}$$

Where, D is the grain size, K is a constant taken to be 0.94, **λ** is the wavelength of the X-ray radiation (1.5406 Å), β is the full width at half maximum and θ is the angle of diffraction. The particle size is calculated for strong three peaks and given in the Table 1.The particle size is found to lie in the range of 7-18 nm. Grain size is found to increase with heat treatment temperature. Annealing treatment allowed conversion of the anatase into rutile-phase. Annealing facilitates the subsequent crystal growth process, accompanied by the diffusion of titania species forming big sized anatase crystals and causing the merging of some adjacent mesopores.

The broad peaks of as prepared sample clearly indicates the minimal crystal size (7 nm). Subsequently on annealing the samples provide diffusion of titania species forming big sized crystals and causing the merging of some adjacent mesopores, so the crystalline size increases to 17 nm for annealed sample.

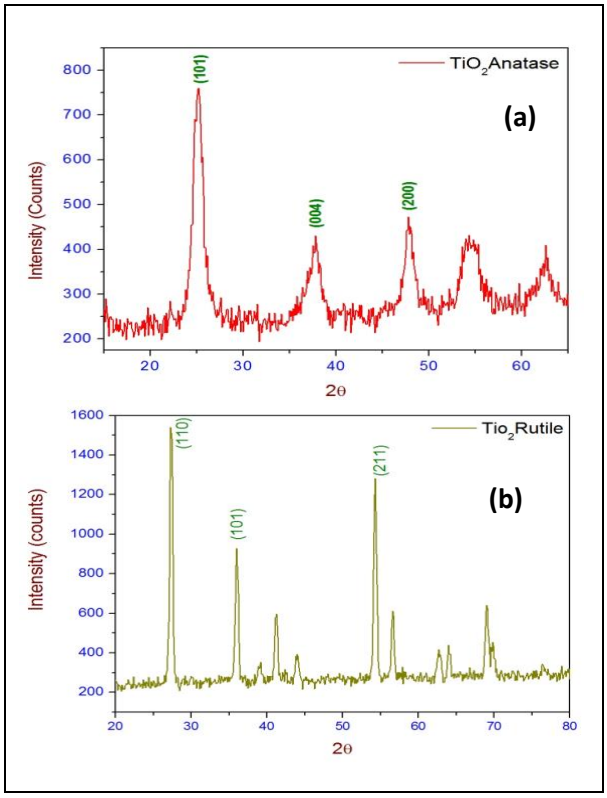

Fig. 1: XRD pattern of TiO_2 nanocrystals prepared as (a) as prepared (b) Annealed at 450 °C

Table 1. Grain size for strongest three peaks

	2theta	FWHM	Grain size nm	Average grain size nm
(a) As prepared	25.0852	1.2505	6.436	6.470
	47.8181	1.1837	7.2599	
	37.6437	1.4510	5.7166	
(b)450°C Annealed	27.3267	0.5058	15.9850	17.298
	54.2562	0.4680	18.8610	
	35.9771	0.4845	17.0480	

Ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I) and compares it to the

intensity of light before it passes through the sample (Io). The ratio I/Io is called the transmittance and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance A= -log (%T/100%).

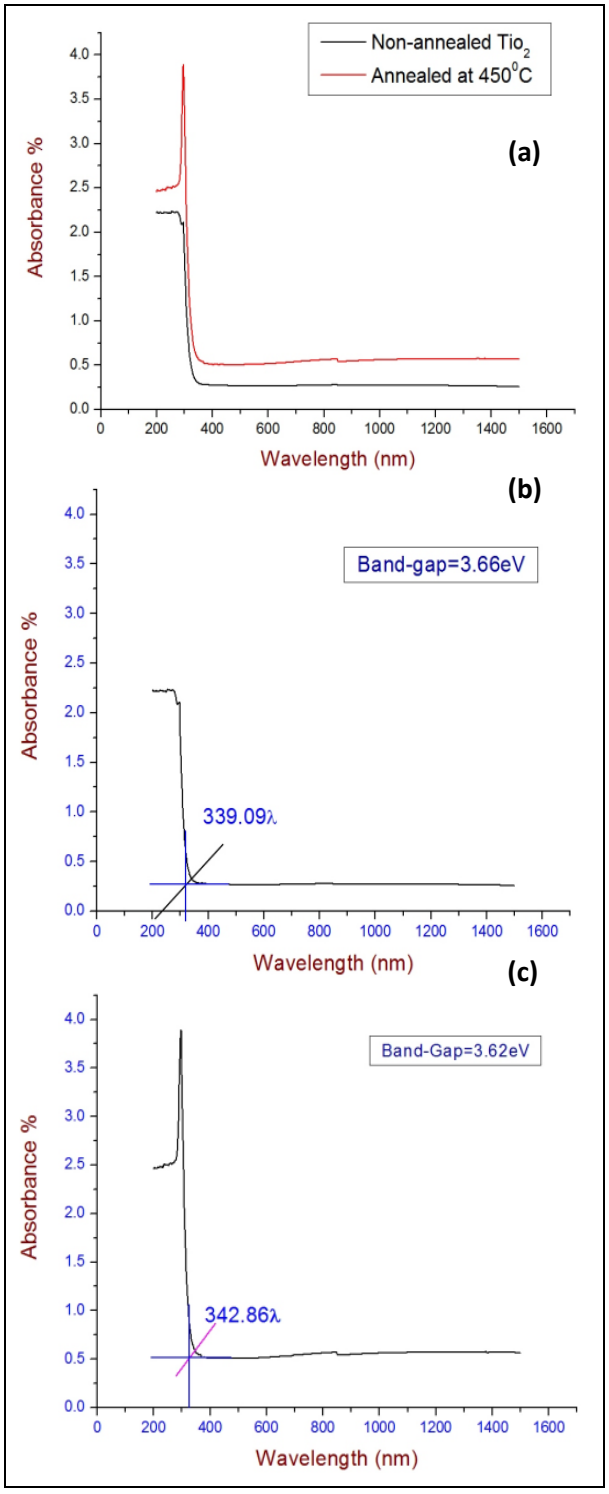

Fig. 2: UV-Vis absorbance spectra for TiO_2 (a) Combined spectra shows a little red shift in wavelength, (b) Bandgap 3.66 eV for as prepared sample, (c) Bandgap 3.62 eV for 450 °C annealed sample

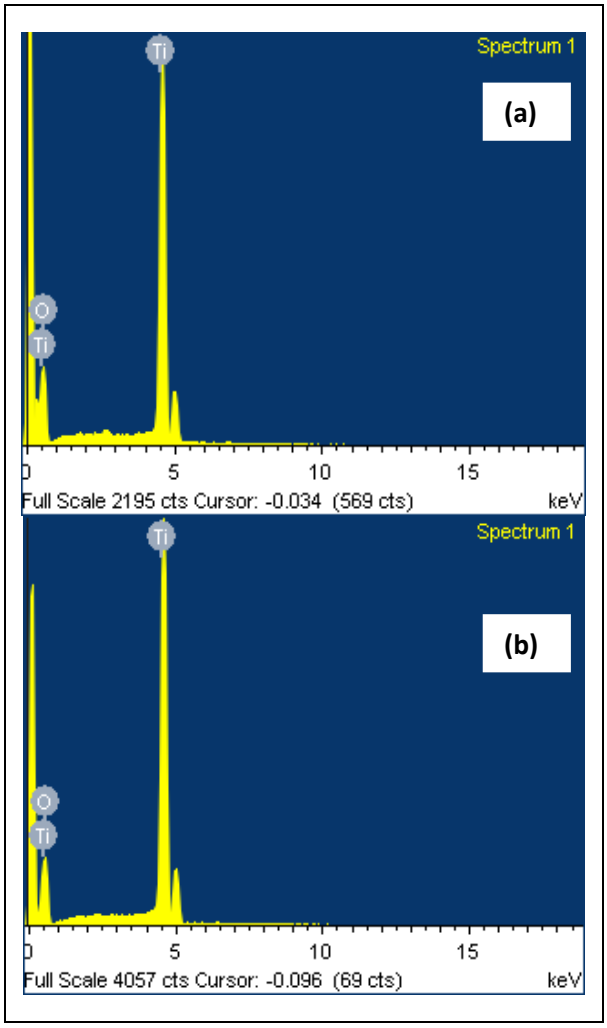

Fig. 3: EDXA spectra of TiO_2 (a) as prepared samples shows more oxide content (b) Annealed sample depicts evaporated oxides

Fig. 2 shows the absorbtion spectra of TiO_2 nano crystals prepared in two different annealing temperatures. The combined spectra in fig. 2(a) depict a smaller wavelength shift towards higher side (redshift) for the annealed sample. This is due to the shift in temperature exposed to the samples, the higher temperature increases the grain size as found in XRD results, thus increased grain size varies the amount of light absorbed on the surface. The bandgap can be determined by examining the absorption of incident photons by the material. Hence the optical properties of the synthesized TiO_2 particles have been evaluated by means of optical absorption spectroscopy.

Tauc method (Senthil *et al.* 2014) is followed to find the bandgap from the absorbance graph. The bandgap energy could be estimated using the formula $Eg = hc/\lambda$, where h and c are the Planck's constant and velocity of light, respectively and the calculated value is 3.66eV for as prepared and 3.62eV for annealed sample.

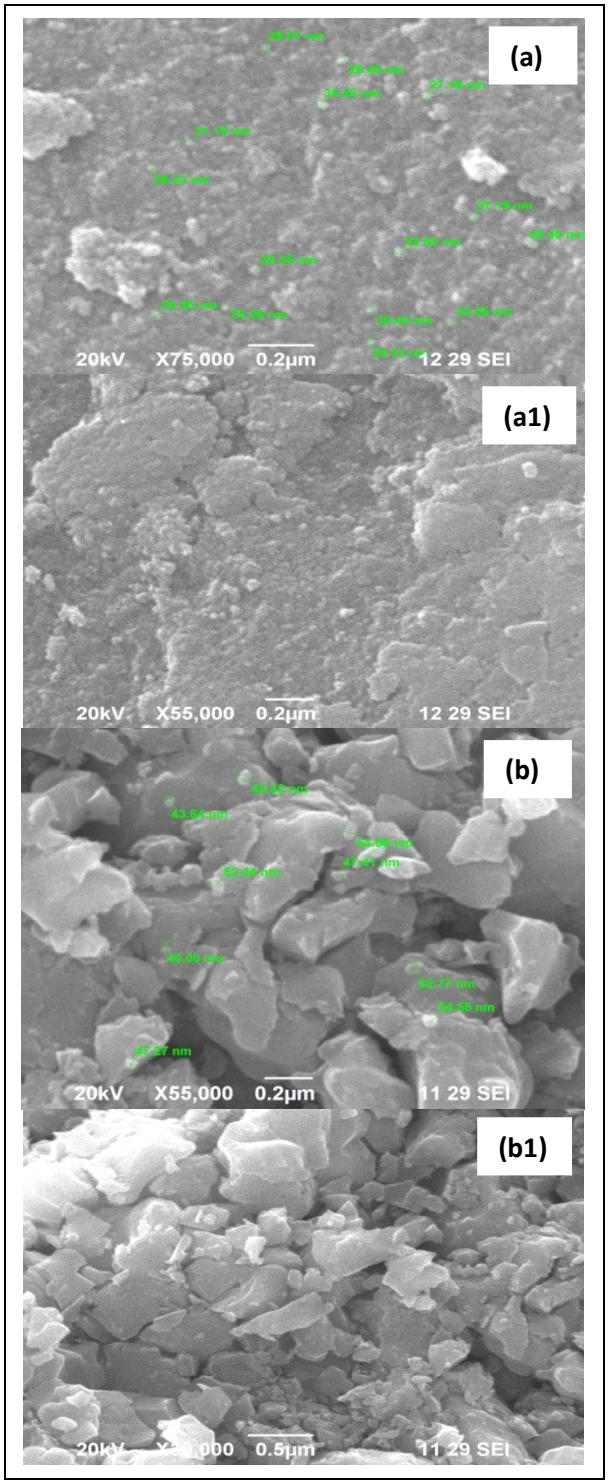

Fig. 4: SEM images of TiO_2 nano crystals prepared by sol-gel, (a & a1) the surface morphology of as prepared TiO_2, (b&b1) Annealed sample surface image

The purity and composition of the synthesized sample has been studied by Energy Dispersive X-ray Analysis (EDXA). Fig. 3 shows typical composition of materials found in the sol-gel prepared sample of TiO_2. Fig. 3(a) shows high peak for oxide than titanium, this is due to the fact, prepared sample possess oxygen contents. Whereas the annealed sample fig. 3(b) shows the oxide content decreased with as prepared. This brings out annealing burns out the oxygen during its process. Apart from titanium and oxide, there is no other trace of materials is found in the spectra. So, the prepared samples are pure and no impurities are present in the samples. The content of titanium is 48.56% and oxide is 51.44% in as prepared sample, whereas the titanium content is 51.89% and oxide content is 48.11% in annealed sample as per EDXA. The surface morphology of the prepared samples and approx grain size was studied using SEM images. The fig. 4(a) shows the rough surface in amalgamation with low particle size for the non annealed sample. The grain size defined by XRD and in the SEM image coordinates with each other. The higher size depicted in SEM image is due to aggregation occurred in the synthesis. The annealed sample fig. 4(b) shows solid and flake like structures with increase in particle size. The increase in size is due to the thermal effect of annealing at 450 °C. This increase in particle size with change in annealing temperature is in agreement with XRD. The surface morphology had witnessed change due to annealing.

4. CONCLUSION

TiO_2 nanocrystals were synthesized from sol-gel method. The prepared TiO_2 is of pure and have no impurities as shown in EDXA. The X-ray diffraction results shows the grain size of TiO_2 nanocrystals increases with annealing temperature and phase of TiO_2 changes from anatase to rutile. This result shows annealing temperature affect the phase and grain size of TiO_2. The UV-Vis absorbance spectra shows red shift towards annealing and bandgap tend to slightly decrease from 3.66 eV to 3.62 eV due to annealing temperature. The SEM image coordinates with the XRD outcome in grain size and structure.

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