

Synthesis of TiO₂ nanocrystalline powder by basic route and its application for dye sensitized solar cell (DSSC)

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Abstract

Herein, the N719 sensitized solar cell characteristics of TiO₂ is presented. The Ti-hydroxide precursor for TiO₂ is prepared by using simple precipitation route in basic conditions at 60 to 70 °C with titanium tetra isopropoxide (TTIP) and sodium hydroxide as starting materials. The as-prepared Ti-hydroxide precursor is annealed at 350 and 450 °C for 2 hr. The as-annealed powders are characterized by using X-ray diffraction (XRD), UV-Visible spectroscopy and scanning electron microscopy (SEM). The XRD studies indicated the formation phase pure TiO₂ powders with anatase symmetry. The morphological studies showed the nanocrystalline nature of the powders. The N719 dye sensitized solar cell is fabricated by using photoanode prepared with 450 °C annealed TiO₂ powder. The dye sensitized solar cell characteristics are found to be $J_{sc} = 1.95 \text{ mAcm}^{-2}$, $V_{oc} = 607 \text{ mV}$, $FF = 0.60$ and $\eta = 0.723 \%$ under illumination with light of 100 mW cm^{-2} intensity.

Keywords: TiO₂; TTIP; Basic route; XRD; SEM; DSSC.

1. Introduction

During last two decades, the dye sensitized solar cells (DSSCs) have become very much popular because of their high photo-conversion efficiency, low fabrication cost and easy manufacturing procedure [1 - 4]. DSSC is a sandwiched assembly of photoanode, dye, iodine based electrolyte and counter electrode. The electron generated with absorption of light by dye is transferred to photoanode and then passed through load reach at counter electrode. Here, the electrolyte plays its role and excited dye is regenerated.

In the recent years, the TiO₂ is found to be very useful material for different applications like photovoltaic cells, photocatalyst, environmental application, water splitting, gas sensors, super hydrophilic and self cleaning [5-7] due to its better thermal stability, biocompatibility, non-toxicity, strong oxidized

stability etc. Among various semiconducting oxides, the TiO_2 has become the an important domain of research because of its better physicochemical properties required for the development of functional devices [8 -11]. Due to high chemical stability, unique photovoltaic and photochemical properties and requisite position in conduction band edge, nanocrystalline TiO_2 is found to be the most possible photoanode candidate for DSSC application. The various physicochemical properties of the TiO_2 greatly depend on the three phases: anatase, rutile and brookite. Among these three phases of anatase TiO_2 is noted to be excellent for catalytic and solar energy conversion application.

The literature survey indicates that several of physico wet-chemical routes like sol-gel hydrothermal, sonochemical microwave etc. are reported for the synthesis of the nanocrystalline TiO_2 powders [12- 18]. However, precipitation technique is easy in operation, cost effective and low temperature processing as compared to the other methods of preparation nanocrystalline TiO_2 . In view of this, a modified simple precipitation technique is used for the preparation of Ti-hydroxide precursor leading to crystallization of nanocrystalline TiO_2 powders on annealing at elevated temperature. This as-prepared nanocrystalline TiO_2 powder is used for making photoanode for dye sensitized solar cell (DSSC) application. The results obtained pertaining to the synthesis, characterization of nanocrystalline TiO_2 powder and DSSC characteristics of TiO_2 photoanode made with this powder are presented in this communication.

2. Experimental

Materials

Titanium tetra isopropoxide (TTIP, Spectrochem., Pune), NaOH (Loba Chem., Pune), Di-tetra-butyl-ammonium cis-bis (isothiocyanato) bis-(2,2-bipyridyl-4,4- dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N719) (Solaronix, Switzerland), 1-vinyl-3-methyl-imidazoliumiodide, LiI, iodine, and 4-tert-butylpyridine in 3-methoxypropionitrile electrolyte (Batsol Chem., Mumbai) were used as precursor materials in present research work without any purification.

Synthesis of TiO_2 powder

The 0.2 M solution of titanium tetra isopropoxide (TTIP) was prepared in isopropanol. The 0.1 M solution of NaOH was prepared in double distilled water (DDW). In basic route, TTIP solution was added slowly drop by drop to the NaOH solution at ice bath temperature. The resultant colloidal solution obtained within 20 min. was filtered using Whatman 41 paper. The resultant precipitate was washed with double distilled water and then filtered. The resultant precipitate was dried at 80 °C for 4 hr. The as-dried hydroxide precursor powder was annealed at 350 and 450 °C for 2 hr. The resultant oxide powders obtained at 350 and 450 °C were identified as BI350 and BI450 respectively.

Characterization of powders

The as-heated resultant BI350 and BI450 powders were characterized by using different physical techniques. The X-ray diffraction patterns of resultant powders recorded by using XRD machine (Rigaku, MiniFlex 600 System, Japan, CuK_α radiation, $\lambda=1.5406 \text{ \AA}$) were used for structural analysis. The microphotographs of resultant powders obtained by using scanning electron microscope (Nova NanoSEM 450, with Energy Dispersive Spectrometer, EDS, Bruker XFlash 6I30) were used for morphological

analysis. The optical spectra recorded by using the UV-Visible spectrophotometer (UV -2600 Shimadzu, Japan) were used to find band gap.

Cleaning of FTO substrate

The fluorine doped tin oxide (FTO) substrates were cleaned in detergent solution. Then ultrasonic washing treatment in double distilled water was given to the substrates for 30 min. After this, again ultrasonic washing treatment in acetone was given to the substrates for 15 min. Then substrates were dried at 100 °C for 1 hr. These thoroughly cleaned FTO substrates were used for the deposition films of resultant as-heated powders.

Fabrication of DSSC

The schematic diagram of as-made dye sensitized solar cell (DSSC) prepared in present work is shown in the fig. 1. The 0.5 gm of the active BI450 powder was pulverized using pestle and mortar. In this powder, the acetic acid solution in water was added drop by drop to obtain the lump free paste. This paste was made suitably viscous by adding the excess ethanol to it. After this, the paste was stirred at 250 rpm for 2 hr magnetically and then sonicated 2 hr. This final paste was used for the preparation of photoanode TiO_2 film. The cleaned FTO substrate was used for the preparation of TiO_2 photoanode film by using Doctor Blade technique. The 4 edges of the FTO substrate were masked with scotch tape leaving 0.15 cm^2 area for film deposition. The as-prepared paste as mentioned above was deposited in the 0.15 cm^2 area by using Doctor Blade technique.

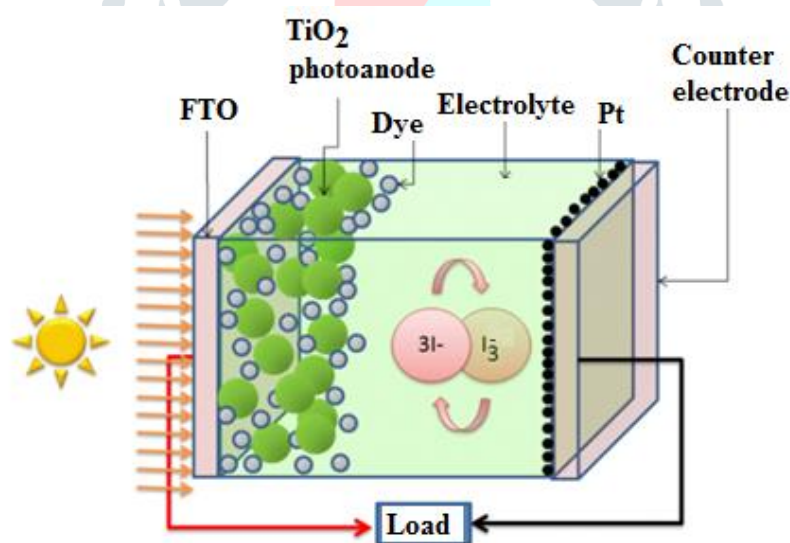


Fig. 1 Schematic diagram for the as-fabricated DSSC

To remove the pinholes if any, the as-deposited film was dried at 60 °C and then annealed at 450 °C for 1 hr. This as-annealed film was used to make photoanode for DSSC. For this purpose, film was kept for 24 hr in 0.5 mM solution of N719 in a mixture containing 1:1 ratio of acetonitrile and ethanol. The colour of film was found to be changed from white to pink yellow. This dye sensitized photoanode film and platinum (Pt) coated FTO counter electrode were assembled into a sandwich type cell with Pt side in contact with sensitized film. The electrolyte solution was prepared with 0.6 M KI, 0.075 M iodine I_2 in a mixture of acetonitrile (20 ml) and ethylene glycol (5 ml). The requisite amount of the electrolyte was inserted between two electrodes: photoanode and counter electrode. This resultant DSSC was used for the measurement of

solar cell properties. The current density (J) - voltage (V) curve for resultant DSSC was obtained by using the solar simulator (Newport Corporation's Oriol® Sol2A® Class ABA solar simulation systems) at 100 mW/cm² power of incident light from the Neon lamp.

3. Results and discussion

Fig. 2 shows the X-ray diffraction (XRD) patterns of the resultant BI350 and BI450 powders. The powder BI350 obtained at 350 °C annealing temperature indicates the amorphous nature. The four broad humps around $\theta = 25^\circ$, 47° , 54° and 63° present in the XRD pattern supported the amorphous nature of the BI350 powder. The powder BI450 obtained at 450 °C annealing temperature shows the well crystalline nature.

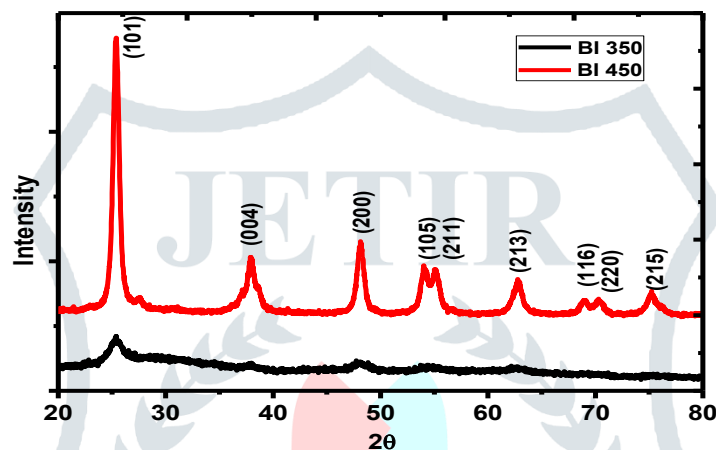


Fig. 2 XRD patterns for BI350 and BI450 as-prepared powders

The (101), (004), (200), (105), (211), (204) and (215) reflections of the anatase TiO₂ phase [JCPDS Card no. 21-1272] are observed in the XRD pattern of the BI450 powder. The XRD pattern of BI450 powder is indexed to anatase (tetragonal) phase symmetry of TiO₂. The reflections for rutile TiO₂ phase are not observed in the XRD pattern. This indicates that BI450 powder is phase pure and contains only TiO₂ particles having anatase (tetragonal) symmetry. The crystallite size for BI450 powder is calculated by using Debye-Scherrer relation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad - (1)$$

where, $\lambda = 1.54 \text{ \AA}$, β = full width at half maximum and θ = Bragg's diffraction angle. The crystallite size is found to be 15.2 nm. It shows the nanocrystalline nature of the particles of BI450 powder. The lattice constants are calculated by using relation:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad - (2)$$

where, d = inter-planer distance. The lattice constants are calculated from the lattice spacing of anatase (101) and (200) reflections. The lattice constants obtained for the BI450 powder are found to be $a = 3.7817 \text{ \AA}$ and $c = 9.4963 \text{ \AA}$. The observed values of lattice constants are found to be matching with reported standard values for anatase tetragonal TiO₂ phase. The Williamson - Hall (W-H) plot (not shown here) is generated from the equation,

$$\beta \cos \theta = \frac{0.9\lambda}{D_w} + 4\varepsilon \sin \theta \quad - (3) \text{ where, } \beta = \text{full}$$

width at half maximum in radians, λ = wavelength of X-rays, θ = diffraction angle, D_w = effective particle size and ε = effective strain. The graph of $\beta \cos \theta$ vs. $\sin \theta$ is linear fitted. The crystallite size (D_w) and lattice strain (ε) are calculated from this equation of line. From the W-H plot, the value of crystallite size for BI450 powder is found to be 30.8 nm. The value of lattice strain (ε) is found to be 0.0045. Qualitatively, the average crystallite size obtained from W-H plot is also in good agreement with the results obtained from Debye-Scherrer's relation (1). Fig. 3 (top) gives the UV-visible absorbance spectra for BI350 and BI450 powders. The corresponding the Tauc plots $[(Ah\nu)^2 \text{ vs. } h\nu]$ for BI350 and BI450 powders obtained from the UV-Visible spectra are presented in fig. 3 (bottom). The band gap energy (E_g) values are obtained by extrapolation of straight-line portion of the plot to zero absorption edge as shown in fig. 3 (bottom). The band gap values (E_g) for BI350 and BI450 powders are found to be 3.37 eV and 3.29 eV respectively. This data is in good agreement with reported values for anatase (tetragonal) TiO_2 . The decrease in band gap energy for the BI450 powder is due to increase in particle size by the use of higher annealing temperature leading to the sintering effect.

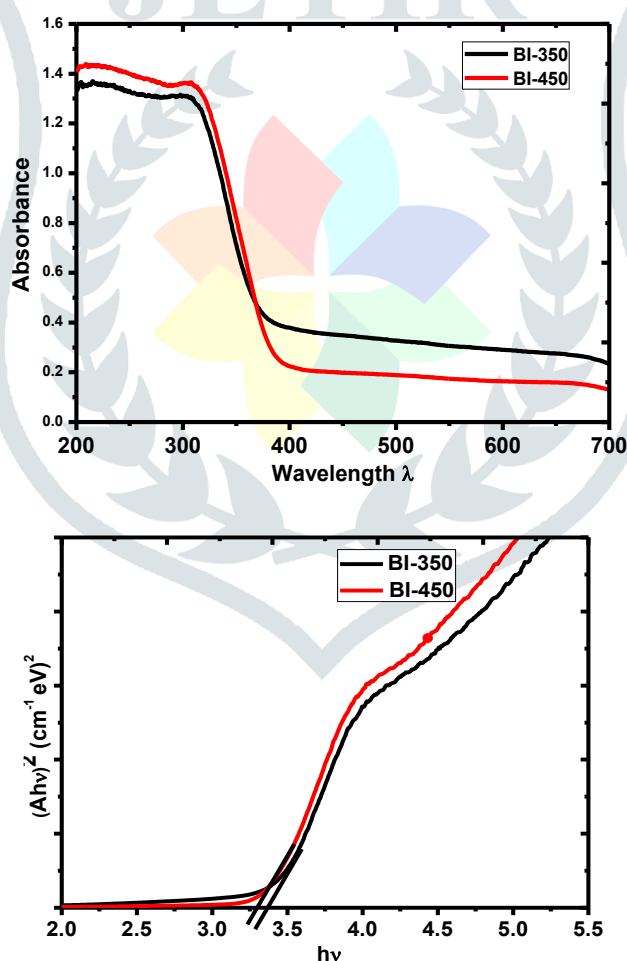


Fig. 3 UV-visible absorbance spectra (top) and corresponding Tauc plots (bottom) for BI350 and BI450 powders

Fig. 4 shows the scanning electron microphotographs for BI350 and BI450 powders. The microphotographs show the primary particles with nearly spherical morphology.

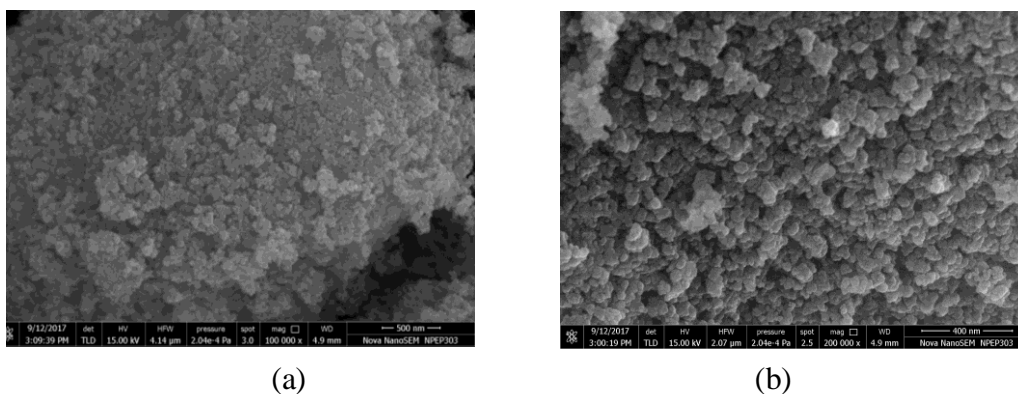


Fig. 4 Scanning electron microphotographs for (a) BI350 and (b) BI450 powders

The soft agglomerates of primary particles are clearly seen in the both microphotographs. In both case, qualitatively, the particle size distribution is found to be nearly uniform. The values of average particle sizes of BI350 and BI450 powders are noted to 30 and 40 nm respectively. The increased particle size in case of BI450 powders is due to sintering effect at higher annealing temperature of 450 °C. This observation is consistent with the results obtained in XRD and UV-visible spectroscopy studies. The powder BI450 with well crystalline nature was used for the preparation of TiO₂ photoanode required for the fabrication of N719 sensitized solar cell as mentioned in the experimental section. Fig. 5 shows the J-V curve for N719 sensitized solar cell made with TiO₂ photoanode of BI450 powder sample.

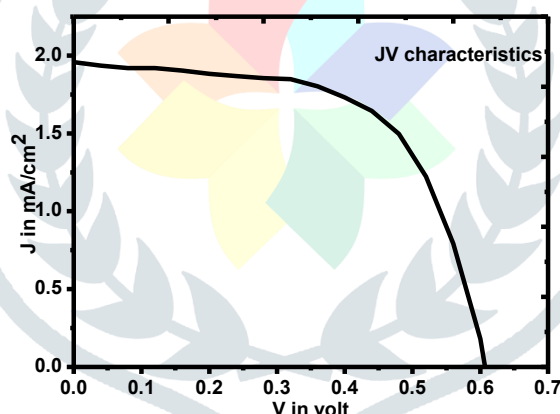


Fig. 5 J-V curve for N719 sensitized solar cell made with TiO₂ photoanode of BI450 powder

Fig. 5 shows that the nature of curve is similar to J-V curve of standard solar cell. The solar cell properties are noted to be (i) short circuit current density (J_{sc}) = 1.95 mA.cm⁻², open circuit voltage (V_{oc}) = 607 mV, fill factor (FF) = 0.60 and photo conversion efficiency (η) = 0.723 % under illumination with of DSSC by light of 100 mW cm⁻² intensity. The colour of 24 hr N719 sensitized TiO₂ is found to be light pink. This is due to lower dye loading capacity of TiO₂ photoanode having inadequate volume porosity. This is might be responsible for giving the moderate photo-conversion efficiency performance to present TiO₂ photoanode made with BI450 powder.

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