Economical Fruit Dye Sensitized Nanocrystalline TiO_2 Photoanode for Solar Cell Fabrication

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Abstract: Dye sensitized solar cell (DSSC) proposed by O'Regan and Grätzel has attracted considerable interest in research since 1991. In present work, solar cell characteristics of pomegranate fruit dye sensitized TiO_2 photoanode is presented. The TiO_2 powders were prepared by using titanium tetra-isoproxide (TTIP) as Ti precursor at temperatures of 300, 400 and 500 ^oC. As-prepared powders were characterized by using X-ray diffraction (XRD), UV-visible spectroscopy and field emission scanning electron microscopy (FESEM). The effect of annealing temperature on structural and optical properties of TiO_2 powders was studied. The pomegranate fruit dye sensitized solar cell (DSSC) characteristics of TiO_2 thick films deposited on FTO coated glass substrates by using Doctor's Blade method were studied by using solar simulator and with polyiodide as an electrolyte. The characterization studies revealed that as-prepared TiO_2 powders were nanocrystalline with anatase phase symmetry. The crystalline sizes of as-prepared TiO_2 powders obtained at 300 and 500 ^oC were found to be 12 and 18 nm respectively. The optical band gap of as-prepared TiO_2 powders obtained at 300 and 500 ^oC were found to be 3.34 and 3.22 eV respectively. The absorption coefficient of resultant was noted to be of the order of 10^4 cm^{-1}. The morphological analysis of resultant powders using SEM revealed spherical TiO_2 particles with sizes between 10 to 50 nm. The pomegranate fruit dye sensitized TiO_2 photoanode showed the solar properties: short circuit current (I_{sc}) = 0.412 mA, open circuit voltage (V_{oc}) = 0.628 V, fill factor (FF) = 39.11 % and photo-conversion efficiency (η) = 0.139 %.

Index Terms - Nanocrystalline, Anatase TiO_2 film, TTIP, DSSC, Pomegranate fruit dye.

1. INTRODUCTION

A new type of solar cells: dye-sensitized solar cells (DSSCs) developed by O'Regan and Grätzel in 1991 have been attracting much attention over last decade as potential low-cost alternative to the commercial silicon based solar cells due to their ease of fabrication and high photo-conversion efficiencies [1],[2],[3]. Titanium dioxide is one of the most promising materials for photochemical energy conversion processes. However, its wide band gaps of 3.0 eV and 3.2 eV for the rutile and anatase phases respectively require UV light for the excitation of electron-hole pairs. This limits its applicability to efficient solar energy conversion because only 5-7 % of the solar spectrum lies in the UV range accessible by pristine TiO_2. TiO_2 nanoparticles explicit the following special properties: (i) greatly enhanced surface area giving effective exposure to light and facilitates the photochemical reactions on the surface, and (ii) enhanced photoinduced charge transport useful for harvesting and donating of photo induced electrons [4],[5]. In literature, the conversion efficiencies are reported in the range of 0.06 to 0.09 % by using natural dye for different materials and no depletion layer formation on the surface, which profoundly changes the photo electrochemical properties [6],[7]. In view of this, the main objective of present work was to fabricate DSSCs based on TiO_2 films and pomegranate and strawberries fruits dyes for their better photovoltaic performance. For this purpose, the nanocrystalline TiO_2 powders were synthesized by simple hydrolysis route followed by annealing treatment. The nanocrystalline TiO_2 powders were characterized by using XRD, Raman spectroscopy, FESEM and UV-Visible spectroscopy. TiO_2 films of these powders were prepared on Indium tin oxide (ITO) substrates by using Doctor's Blade method. The resultant films were used as photoanodes for pomegranate and strawberries fruits dyes sensitized solar cell applications. The results obtained with respect to the above mentioned objective are presented in this paper. The data pertaining to this is presented in this communication.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of TiO_2 powder

A 25 ml of titanium tetra-isopropoxide, TTIP ($C_{12}H_{28}O_4Ti$) was slowly added to double distilled water (DDW). The hydrolysis of TTIP was carried out under vigorous stirring at room temperature (RT) for 2 hr. A white precipitate formed was washed with DDW for several times by using centrifuge. The precipitate was dried at room temperature for 1 hr and then at 100 ^oC in an electric oven for 1 hr. This as-dried precipitate was annealed at 300, 400 and 500 ^oC for 2 hr.

2.2. Physical characterization of TiO_2 powder

The resultant as-annealed powders were characterized by using different physical techniques. The X-ray diffraction patterns of resultant powders were recorded by using Bruker D8 Advance (filtered CuKα radiation, λ = 1.5406 Å) machine. Raman spectra were recorded by Jobin Yvon Horibra LABRAM-HR (single mode Ar-ion laser for excitation λ = 488 nm) spectrometer. The average thickness of the films of resultant powders measured by using surface profiler [KLA Tencor P -16+] was found to be 10.23 µm. The optical spectra of films were recorded by using the UV-Visible spectrophotometer [V-670, JASCO UV-VIS-NIR spectrometer]. The morphological analysis of powders was done by using field emission scanning electron microscope (Nova NanoSEM 450, with Energy Dispersive Spectrometer, EDS, Bruker XFlash 6I30).

2.3. Preparation of TiO_2 films by using Doctor's Blade method

The as-annealed powders were used for the preparation of respective films on thoroughly cleaned conducting fluorine tin oxide (FTO) glass substrates by using Doctor's Blade method. Initially, FTO substrates were washed with detergent and DDW. The substrates were boiled in concentrated chromic acid (0.5 M) for 1 hr and then kept in it for 5 hr. After this, the substrates were rinsed with DDW and then ultrasonically cleaned in acetone for 15 min. Finally, the substrates were rinsed with acetone and then dried under IR lamp. The 0.50 gm of as-heated powder was ground with 0.25 gm of polyethelyene glycol (PEG, M.W. = 20,000) by using pestle-mortar and by adding few drops of dilute acetic acid for 30 min. to produce a lump free paste. Three edges of thoroughly cleaned FTO substrate was masked with TISCO tape by keeping the area = 0.25 cm^2 free for the deposition of the film. The thickness of tape loaded over the substrate was around 10 µm. The unmasked region of FTO substrate was completely filled with the as-annealed powder. This film was dried under halogen lamp for 30 min. Finally, these resultant films were subjected as photoanode for the fabrication of dye sensitized solar cells (DSSCs).

2.4. Preparation of Dye

The 250 gm of nuts of Pomegranate was crushed in 2 ml deionized distilled water and filtered for 5 times. The filtered quantity was used as dye for DSSC. Similarly, 250 gm of nuts of strawberry was crushed in 2 ml deionized distilled water and filtered for 5 times. The filtered quantity was used as dye for DSSC.

2.5. Fabrication of dye sensitized solar cell (DSSC)

The resultant film of TiO_2 was initially kept in pomegranate dye for 24 hr at room temperature. This dye sensitized film was used as photoanode. The counter electrode; FTO coated with carbon was placed on the top of dye loaded film. This sandwich was used as DSSCs. The few drops of polyiodide electrolyte solution were poured in this sandwich from exposed side of resultant film (side of film not masked with tape). The current (I) - voltage (V) characteristic curves for different DSSCs (area = 0.25 cm^2) illuminated under standard AM1.5 simulated sunlight (power density of 100 mW/cm^2) were recorded by using solar simulator (Newport Corporation's Oriel® Sol2A® Class ABA solar simulation systems).

3. RESULTS AND DISCUSSION

3.1. Structural properties

3.1.1. XRD studies

Fig. 1 shows the XRD patterns recorded for as-dried precipitate annealed at 300, 400 and 500 ^oC in air for 2 hr. The powders showed several diffraction peaks at 2θ = 25.2, 48 and 54.1^o with the inter-planar spacing of 3.53, 1.89 and 1.69 Å respectively. The relative peak intensities of these diffraction peaks also increase as the annealing temperature increases. The evolution of phase is started at 300 ^oC. The powders annealed at 400 and 500 ^oC clearly indicate the anatase (tetragonal) phase of TiO_2 since all the reflections are found to be perfectly matching with the peaks given in the JCPDS data file for anatase TiO_2 [PDF-21-1272]. The peak corresponding to the (101) plane became sharper and the full width at half-maximum (FWHM)

decreased indicating thereby better crystallinity and an increase in grain size with increasing annealing temperature [8], [9]. The crystalline size of the samples is estimated by the Scherer's formula [10].

$$D = (0.9\lambda)/(\beta \mathrm{Cos}\theta) \quad (1)$$

From equation (1), the values of crystalline size from the XRD peak (101) with $2\theta = 25.2^{o}$ for the powders annealed at 300, 400 and 500 ^{o}C were found to be 12, 14 and 18 nm respectively. After heat treatment at 300 ^{0}C, TiO_2 powder exhibits anatase phase with moderate crystal growth. Hence, the nanocrystallinity of powder depends on deposition parameters especially on annealing temperature.

3.1.2. Raman spectra

Fig. 2 shows the Raman spectra of the as-dried precipitate annealed at 300, 400 and 500 ^{o}C in air for 2 hr. The results of X-ray diffraction analysis are supported by the Raman spectra of TiO_2 powders. The Raman spectra three powders show well defined peaks and the absence of overlapping peaks confirming thereby that the powders are well crystallized with low number of imperfect sites. Anatase TiO_2 has six Raman active modes: $A_{1g} + 2B_{1g} + 3E_g$. For single crystal TiO_2, the following allowed bands: 142 ± 2 cm^{-1} (E_g), 194 ± 3 cm^{-1} (E_g), 393 ± 2 cm^{-1} (B_{1g}), 512 ± 1 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}) and 634 ± 2 cm^{-1} (E_g) are reported in literature [11]. Four distinct peaks (Fig. 2) are observed in the Raman spectra of the TiO_2 powders. These peaks can be assigned according to the above given allowed modes of anatase TiO_2. The observed peaks have bands centered at 142.9 cm^{-1} (E_g), 396.5 cm^{-1} (B_{1g}), 517.3 cm^{-1} (A_{1g}) and 634.6 cm^{-1} (E_g). The lowest-frequency E_g mode at 142.9 cm^{-1} is the strongest of all the observed modes in anatase TiO_2 nanocrystals. It's shift is quite close to 142 ± 2 cm^{-1} in anatase phase of single-crystal. The Raman spectra show that the as-prepared TiO_2 nanocrystals are well crystallized in the anatase structure. The results of the Raman studies confirm the well crystallization TiO_2 powders obtained simple hydrolysis method followed by annealing at moderate temperature and hence these powders are suitable for the fabrication of TiO_2 based dye sensitized solar cells [12].

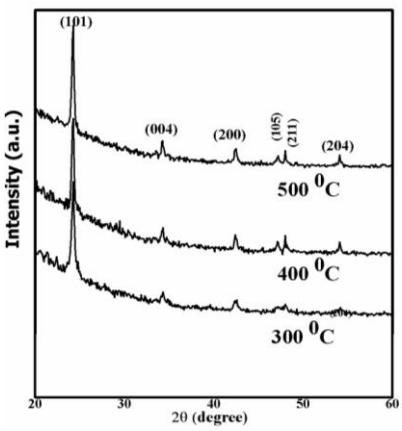


Fig. 1 XRD patterns for resultant powders obtained at different temperatures

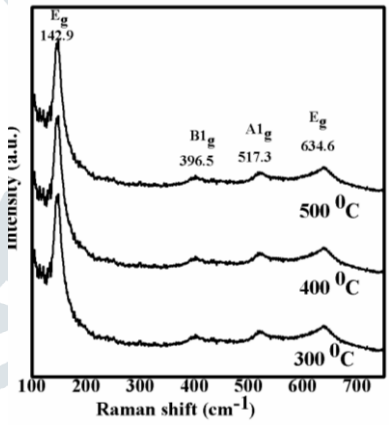


Fig. 2. Raman spectra for resultant powders obtained at different temperatures

3.1.3. Morphological studies

Fig. 3 shows field emission scanning electron microscopy (FESEM) photograph of the film of TiO_2 powder obtained at 400 ^{o}C. From Fig. 3, it is observed that the film is composed of an open porous structure. This is also reflected by the enlargement of the refractivity. The FESEM image shows the following observations: (i) particles are spherical, (ii) particle size distribution is nearly uniform, (ii) particles are soft agglomerates in nature, (iv) each spherical agglomerate contains many particles in the nanometric range and (v) the agglomerate size is in range of 10 and 50 nm. The image also reveals the porous/less densification nature of the film at the surface. The voids are clearly seen at the surface of the film.

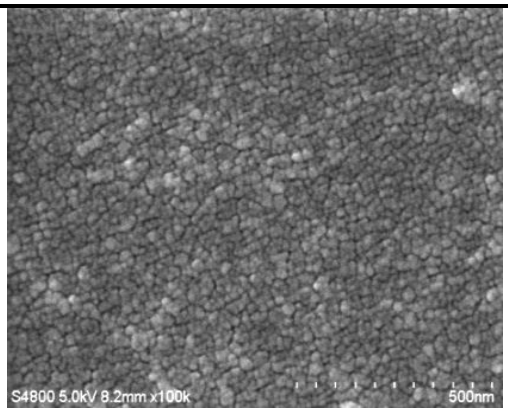


Fig. 3 Field emission scanning electron microscopy (FESEM) photograph of the film of TiO_2 powder obtained at 400 ^oC.

3.2. Optical properties

3.2.1. Transmittance characteristics

The optical transmittance spectra of as-dried precipitate annealed at 300, 400 and 500 ^oC in air for 2 hr are shown in Fig. 4. The TiO_2 powders exhibit high transmittance annealed at 400 ^0C is 74 % at 675 nm [13],[14]. All powder showed good transmittance in the visible wavelength regions.

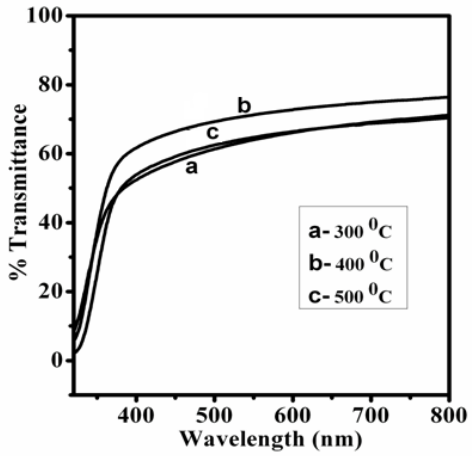


Fig. 4 Transmittance spectra of the nanocrystalline TiO_2 powders obtained at different temperatures

3.2.2. Optical band gap

The optical band gap of the TiO_2 powder was determined by using Tauc's relation [15].

$$(\alpha h\upsilon)^{1/2} = A(h\upsilon - E_g) \quad (2)$$

where, α = absorption coefficient, A = constant independent of photon energy and hυ = energy of excitation. The value of E_g is obtained by extrapolation of the straight-line portion of the plot to zero absorption edge in a graph of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ as shown in Fig. 5 The linear part of the plot is extrapolated towards lower energies. The intercept on the energy axis is noted down. It is found from Tauc's plots for TiO_2 powders that band-to-band indirect transitions are most probable than the direct transitions [9], [16], [17]. The values of optical band gap of TiO_2 powders obtained at 300, 400 and 500 ^oC are found to be 3.34, 3.27, and 3.22 eV respectively. The optical band gap of the TiO_2 powder is found to be decreasing with increasing the annealing temperature.

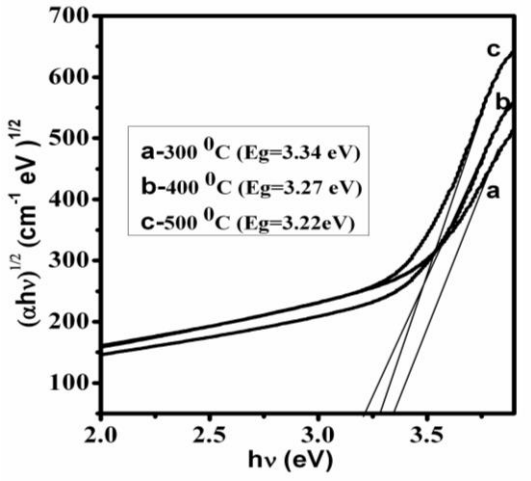
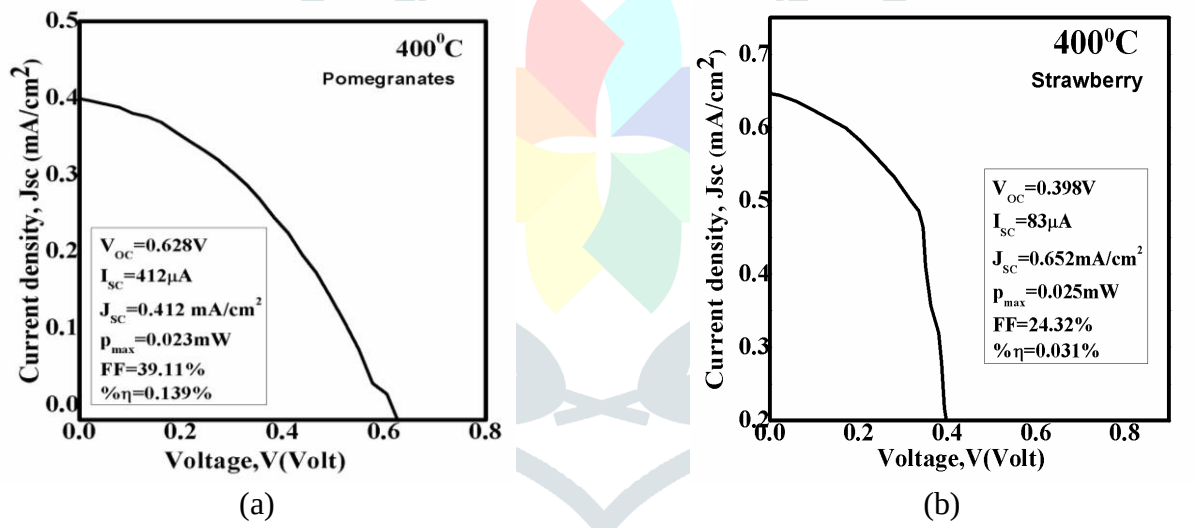


Fig. 5 Variation of $(\alpha h\nu)^2$ vs. hν of nanocrystalline TiO_2 powders obtained at different temperatures.

3.3. Photovoltaic properties

The TiO_2 powder obtained at 400 ^oC annealing temperature and having better optical properties was used for the study of dye sensitized solar cell characteristics. As-mentioned in the experimental section, this powder was used to prepare TiO_2 photoanodes for DSSC application. The solar cell properties of the TiO_2 photoanode sensitized with pomegranate dye are found to be short circuit current (I_{sc}) = 0.412 mA and open circuit voltage (V_{oc}) = 0.628 V, Fill factor (FF) = 39.11 % and photo-conversion efficiency (η) = 0.139 % as shown in fig. 6 (a). The solar cell properties of the TiO_2 photoanode sensitized with strawberry dye are found to be short circuit current (I_{sc}) = 0.083 mA and open circuit voltage (V_{oc}) = 0.398 V, Fill factor (FF) = 24.32 % and photo-conversion efficiency (η) = 0.031 % as shown in fig. 6 (b).



(a) (b)

Fig. 6 J-V plots for (a) pomegranate and (b) strawberry dye sensitized TiO_2 photoanodes made using powders obtained at 400 ^oC.

4. CONCLUSIONS

TiO_2 powder is prepared by simple hydrolysis method followed annealing at moderate temperature. It is simple, cheap and versatile route. The method useful for the synthesis of pure nanocrystalline TiO_2 powders with anatase (tetragonal) symmetry. The TiO_2 particles with spherical morphology and uniform size distribution of TiO_2 particles are formed as a result of this preparation. This nanocrystalline anatase TiO_2 powder is found to be useful for the making photoanode for solar cells sensitized with economical dyes obtained from pomegranate and strawberry fruits.

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