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Natural Dye Extracts of Areca Catechu Nut as dye Sensitizer for Titanium dioxide Based Dye Sensitized Solar Cells

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A dye sensitized solar cell was fabricated using titanium dioxide nano particles sensitized by a new natural dye extracted from areca catechu nut. The natural dye extract contains tannin which is rich in gallotannic acid. The pure titanium dioxide nano particles in anatase phase were synthesized by sol-gel technique and were sensitized by the natural dye to yield photo anode material. The Powder X-Ray Diffraction, UV-vis spectra, Fourier Transform Infra Red spectroscopy, Energy Dispersive X- Ray spectroscopy and Scanning Electron Microscopy studies of pure and natural dye sensitized TiO_2 were carried out to analyze their structural, optical, functional group, compositional and morphological details. The dye sensitized solar cell was fabricated using TiO_2 nano particles coated on FTO glass plate which is sensitized by the natural dye as photo anode and platinum coated FTO as counter electrode. The natural dye sensitized solar cell showed a solar light energy to electron conversion efficiency of 0.76 %.

Keywords: Dye sensitized solar cell, TiO_2, Sol-gel, Areca catechu nut.

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1. INTRODUCTION

Dye Sensitized Solar Cell (DSSC) is a promising source for sustainable development and clean energy for the future due to merits, like low cost, choice of color and design, easy fabrication, environment friendly etc. [1]. The DSSC consists of a dye sensitizer, a metal oxide semiconductor, an electrolyte and transparent conductors which are responsible for determining the efficiency. The solar light was absorbed by the sensitizer which is available on the surface of the metal oxide semiconductor. Charge separation takes place at the interface due to the photo-induced electron injection from dye to the conduction band of the semiconductor [2]. The dye molecule is regenerated by a redox (I^{+} / I_{3} –) system, which itself is regenerated at the counter electrode by passing electrons through the load [3]. This photoelectric process is in contrast with the conventional silicon based solar cells, where the metal oxide semiconductor performs both the task of light absorption and charge separation [4]. Titanium dioxide (TiO_2) is the most successful semiconductor used in DSSC due to its superior properties. The photo electric behavior of TiO_2 was dependent on its crystalline nature, defects on the surface, photon absorption ability, particle size and surface area [5]. The photo sensitizer can be a natural or a chemical one. The chemical dyes have higher life time and light to electron conversion efficiency. Due to their toxic and high synthesis cost, the natural dyes gained much attention. The natural dyes are very cheap, available in plenty and environment friendly [6]. In the present work, we have given first priority to green energy production by using a new natural dye extracted from areca catechu nut as photo sensitizer for the fabrication of DSSC. Using sol-gel hydrolysis route, TiO_2 nano particles in anatase phase were synthesized and sensitized by the natural dye. The natural dye sensitized TiO_2 nano particles based DSSC showed solar light energy to electron conversion efficiency of 0.76 %.

2. EXPERIMENTAL

2.1 Dye Extraction

Areca nut is the seed of a fruit from the tropical palm, areca catechu Linn. The unripe fruit is green and gets reddish yellow color when ripens. Areca catechu nut contains tannin, gallic acid, catechin, alkaloids, fat, gum etc. The predominant pigment of areca catechu is gallotannic acid. The areca catechu nut and the structure of gallotannic acid are shown in Fig. 1. The outer cover of the fresh areca catechu nut is removed and the hard flesh part cleaned, dried and cut into small pieces. The aqueous extract was prepared by the addition of 250 gram of small pieces of dry fruits with 100 mL of distilled water and kept for 8 hours. The mixture was filtered; a dark brown extract was collected and used as a dye sensitizer.

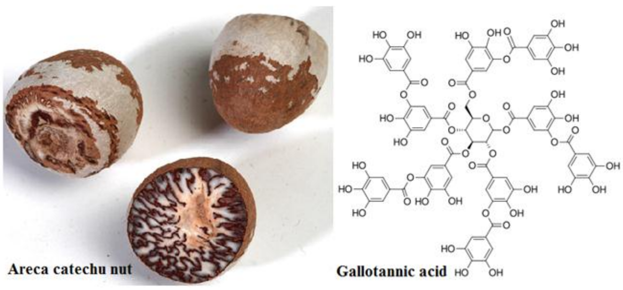

Fig. 1 – Areca catechu nut and structure of Gallotannic acid

2.2 Synthesis of TiO_2

Pure TiO_2 nano particles were synthesized by sol-gel technique by taking titanium isopropoxide (Sigma – Aldrich) as titanium precursor and a mixed solution of distilled water with an alcohol as hydrolysis medium to yield TiO_2 nano particles. A 250 mL solution of distilled water with 15 mL isopropanol (Merck) was mixed thor-

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oughly and the initial pH was noted to be 8.75. The pH of the solution has strong influence on the formation and size distribution of nano particles. When the pH level of the solution is higher than 2, a white suspension of rough precipitants is formed immediately. On the other hand, when the pH level of the solution is 2, a homogeneous suspension of fine particles is formed. Hence, the pH value was adjusted to 2 by adding nitric acid. This solution was stirred vigorously and 5mL titanium isopropoxide solution was added drop wise to result a white precipitation. After the hydrolysis process was over, the turbid solution containing TiO_2 precipitation is heated up to 80 °C for about 2 to 3 hours. After this, the mixture was kept for aging for one hour at room temperature. This yields a high viscous white suspension which is washed in distilled water first and then in ethanol to remove the byproduct impurities. Then, the prepared white precipitate was dried at 100 °C for 10 to 15 hours to obtain fine particles of pure TiO_2.

2.3 Fabrication of DSSC

The pure TiO_2 obtained by sol-gel technique was made into a paste using titanium isopropoxide solution. A thin film was coated using "doctor-blade" method on FTO glass plate. The dried TiO_2 coated glass plate was sintered at 450 ºC for 30 minutes to improve the electronic contact between the TiO_2 nano particles. The photo anode was soaked in areca catechu nut dye for 3 hours to adsorb dye onto the TiO_2 surface. A platinum coated FTO glass plate was used as counter electrode. The liquid electrolyte (I^+ / I_{3-}) was poured in between the two electrodes carefully. The two electrodes were joined together with dye sensitized TiO_2 at the middle without creating air bubbles to prepare natural dye sensitized TiO_2 based DSSC.

3. RESULTS AND DISCUSSION

The powder X-ray diffraction (PXRD) studies were carried out using ISO DEBYEFLEX 2000 diffractometer employing CuKα radiation of 1.531841 Å. The Powder XRD pattern of natural dye mixed TiO_2 nano particles calcined at 250 ºC is shown in Fig. 2. The nano crystalline anatase structure was confirmed by the

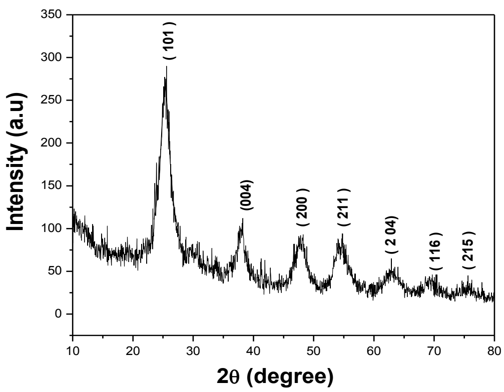

Fig. 2 – Powder XRD pattern of dye mixed TiO_2 calcined at 250 ºC

presence of (1 0 1), (0 0 4), (2 0 0), (2 1 1), (2 0 4), (1 1 6) and (2 1 5) diffraction peaks. The particle size was calculated by Debye-Scherrer's formula, $D = K\lambda / (\beta\cos\theta)$, where, D is the particle size; λ is the wavelength of the X-ray radiation ($\lambda = 0.15406$ nm) for CuKα; K is usually taken as 0.94 and β is the line width at half-maximum height [7]. The particle size obtained using this formula is approximately 42 nm.

The UV-vis absorption spectrum was recorded in the wavelength range from 300 to 800 nm using Shimadzu Model 1601 spectrophotometer. The absorption spectra of pure and natural dye sensitized TiO_2 nano particles are shown in Fig. 3. From the spectra, the pure TiO_2 nano particle's cutoff wavelength is 356 nm. The band gap energy can be calculated using the relation, $E_g = 1239.8 / \lambda$, eV with λ in nm [8] and is calculated as 3.48 eV. The band gap of normal or bulk TiO_2 is 3.2 eV and this variation is due to the change in particle size [9]. The band gap increases with decreasing particle size and the absorption edge is shifted to a higher energy with decreasing particle size. The absorption spectrum of natural dye sensitized TiO_2, shown in Fig. 3, proves the enhanced light photon absorption and extension of absorption region due to the adsorption natural dye on the TiO_2 surface. This can be attributed to the injection of charge into the conduction band of TiO_2 and also by the type of attraction between the sensitizer and its anchoring group with TiO_2 [10]. The dye structure of gallotannic acid dye possesses several C = O and – OH groups which are capable of anchoring on to the Ti sites in the TiO_2 surface. The cutoff wavelength of natural dye mixed TiO_2 is 405 nm and the band gap is found to be 3.06 eV. The band gap of TiO_2 is related to the wavelength range absorbed and the band gap decreases with increasing absorption wavelength [8]. The absorption study reveals the enhancement of photo sensitization behavior of the TiO_2 nano particles due to the adsorption of natural dye.

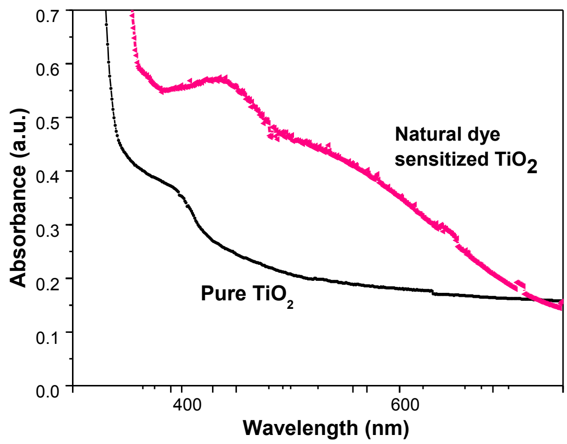

Fig. 3 – Absorption spectra of pure and natural dye sensitized TiO_2

The Fourier Transform Infra Red spectra of pure and natural dye mixed TiO_2 are shown in Fig. 4a and Fig. 4b respectively. Both spectra have the characteristic vibration of Ti – O bond at 646 cm^{-1} and 649 cm^{-1} which normally occur in between the standard range of 450-1000 cm^{-1} [11]. This confirms the formation of TiO_2 nano particles in both samples. The absorption peaks at 1623 cm^{-1} in pure and natural dye mixed TiO_2 is assigned to O – H bending modes [12]. The absorption peaks at 1102 cm^{-1}, 1473 cm^{-1} and 1772 cm^{-1} in natural dye mixed TiO_2 are assigned to the functional groups C – O – C, C – H and C = O respectively [13]. The absorption peaks between 3000 cm^{-1} and 3800 cm^{-1} in pure and natural dye mixed TiO_2 is assigned to O – H stretching vibration mode of water molecules [14].

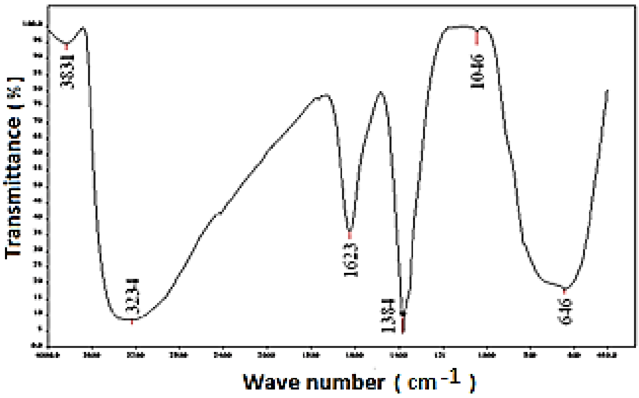

Fig. 4a – FTIR spectrum of pure TiO_2

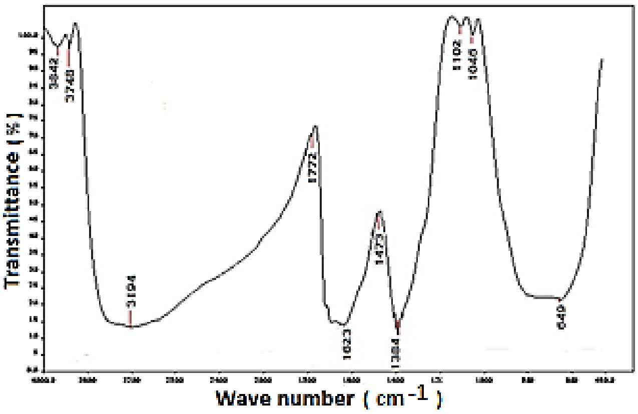

Fig. 4b – FTIR spectrum of natural dye sensitized TiO_2

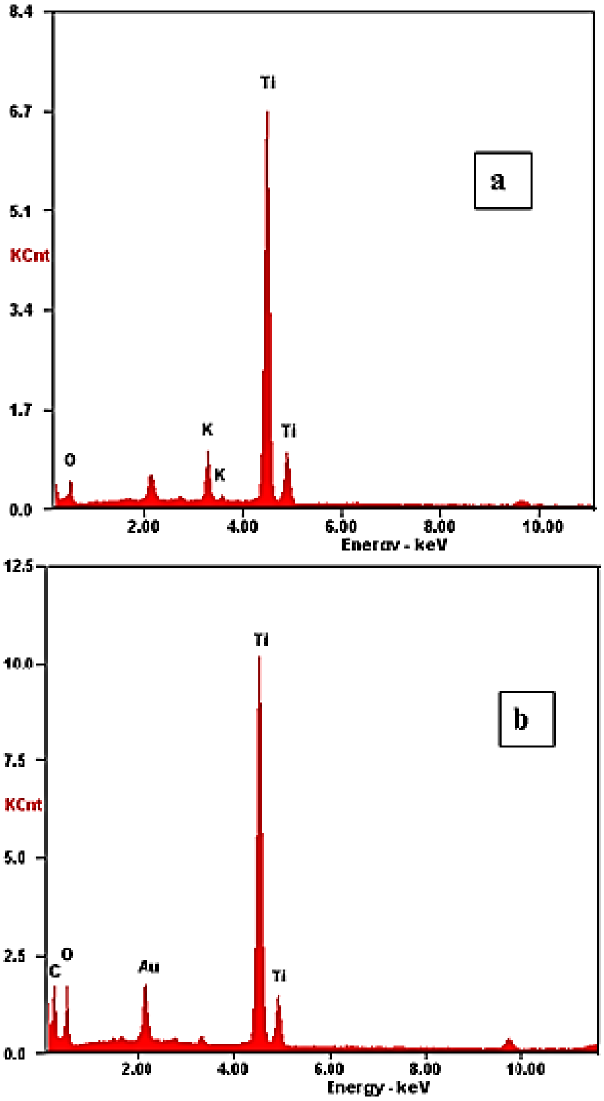

Fig. 5 – E-DAX spectra (a) pure TiO_2 (b) TiO_2 mixed with natural dye

The Energy Dispersive X-ray (E-DAX) spectrum of TiO_2 nano particles is given in Fig. 5a. The spectrum has prominent peaks of Ti and O. From the peaks, it is confirmed that the nano particles synthesized by sol-gel technique belongs to pure TiO_2. The weight contributions are 33.83 and 61.45 percentage for Oxygen and Titanium respectively. Together they contribute 95.28 percentage of the total weight. This indicates the purity of TiO_2 as there is no impurity material presence. The E-DAX spectrum of TiO_2 nano particles mixed with natural dye is shown in Fig. 5b. The weight contributions are 30.51, 30.50 and 29.84 percentages for Oxygen, Titanium and natural dye functional group (COO) respectively. As a whole, they contribute 90.85 percentage of the total weight and confirm the adsorption of natural dye on TiO_2 surface.

The FEI Quanta FEG 200-High Resolution Scanning Electron Microscope with a resolution of 1.2 nm was used to study the morphological properties. The Scanning Electron Microscope (SEM) images of pure and natural dye mixed TiO_2 are shown in Figs. 6a and 6b respectively. The pure TiO_2 nano particles have agglomerated together to form nano clusters. These nano clusters will affect the photo catalytic behavior of TiO_2 as a photo anode material in DSSC. The agglomeration has reduced to a great extent due to the adsorption of natural dye on TiO_2 surface. The morphology has improved as nearly spherical particles and the nano clusters are reduced. The average crystalline size of TiO_2 nano particles is 35 nm and it is closer with the value obtained from PXRD.

The current-voltage (I-V) characteristics of the solar cells were studied using Keithley 2400 source meter with a Xenon lamp of 100 mWcm^{-2} as solar simulator at standard AM 1.5 illumination. The I-V response of the areca catechu nut natural dye sensitized DSSC under the AM 1.5G illumination at 100 mW/cm^2 is shown in Fig. 7.The pure TiO_2 obtained by sol-gel technique was made into a paste using titanium isopropoxide solution. This pure TiO_2 was coated on FTO glass as a thin film using the doctor-blade technique. Then, it was dipped into the natural dye solution for 6 hours to adsorb more dye onto the TiO_2 surface. A platinum coated FTO glass plate was used as the counter electrode. The liquid electrolyte (I^+ / I_{3-}) was placed in

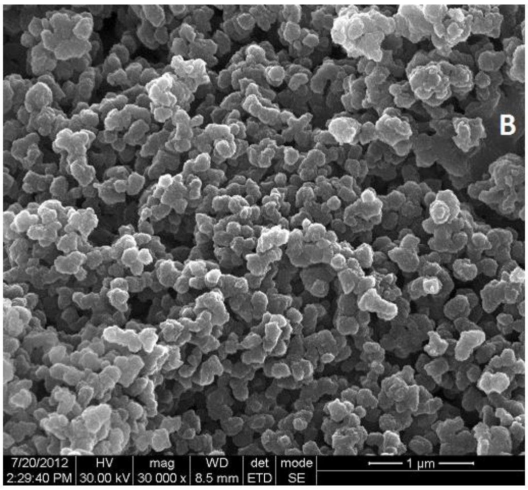

Fig. 6a – SEM Image of pure TiO_2

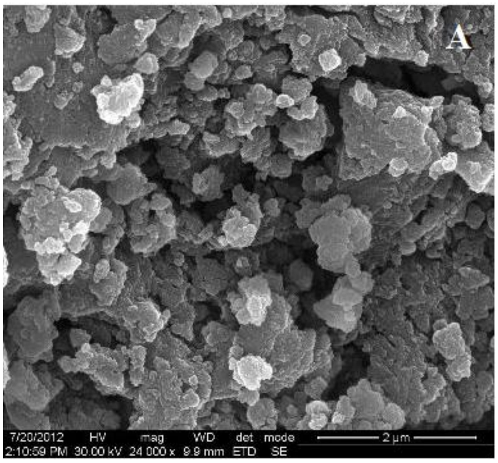

Fig. 6b – SEM image of natural dye sensitized TiO_2

between the two electrodes. The fill factor (FF) was found using the relation,

$$FF = (I_{max} \times V_{max}) / (I_{sc} \times V_{oc})$$

Where, I_{max} and V_{max} denote the maximum output value of current and voltage respectively, and I_{sc} and V_{oc} denote the short circuit current and open circuit voltage respectively. The values of $J_{sc} = 2.6$ mA cm^{-2}, $V_{oc} = 0.52$ V and the calculated value of FF is 56. The total energy conversion efficiency was calculated using the relation,

$$\eta = (J_{sc} \times V_{oc} \times FF) / P_{in}$$

where, P_{in} denotes the energy of incident photon.

The efficiency of natural dye sensitized DSSC was calculated as 0.76 %.

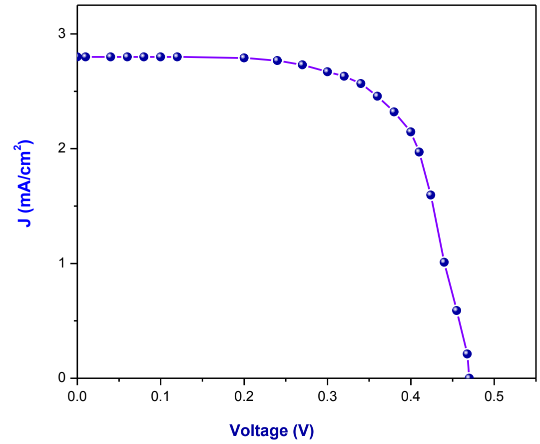

Fig. 7 – I-V characteristics of natural dye sensitized TiO_2 based DSSC

4. CONCLUSION

A new natural dye extracted from areca catechu nut was successfully used as dye sensitizer for TiO_2 nano particles based DSSC. The anatase phase of TiO_2 nano particles calcined at 250 °C was confirmed by PXRD analysis and the average crystalline size is 42 nm. The UV-vis spectra reveals the cutoff wavelength of pure and natural dye mixed TiO_2 as 356 nm and 405 nm respectively. The band gap of natural dye mixed TiO_2 is reduced to 3.06 eV compared to 3.48 eV of pure TiO_2. The FTIR spectra confirm the functional groups of pure and natural dye sensitized TiO_2. The E-DAX study confirms the formation and purity of TiO_2. The SEM images confirm the improvement in morphology due to mixing of natural dye. The light to electron conversion efficiency of natural dye sensitized TiO_2 based DSSC is 0.76 %.

REFERENCES

1. Yasuhiko Takeda, Naohiko Kato, Kazuo Higuchi, Akihiro Takeichi, Tomoyoshi Motohiro, Syungo Fukumoto, Thoshiyuki Sano, Tatsuo Toyoda, *Sol. Energ. Mat. Sol. C.* **93**, 808 (2009).
2. K. Kalyanasundaram, M. Graetzel, *Curr. Opin Biotechnol.* **21**, 298 (2010).
3. M. Graetzel, *J. Photochem.* **4**, 145 (2003).
4. M. Graetzel, *J. Photochem.* **164**, 3 (2004).
5. O'Regan, M. Graetzel, *Nature* **353**, 737 (1991).
6. Jin Tang, Sanyin Qu, Juan Hu, Wenjun Wu, Jianli Hua, *Sol. Energ.* **86**, 2306 (2012).
7. B. Li, X. Wang, M. Yan, L. Li, *Mater. Chem. Phys.* **78**, 184 (2002).
8. Noshin Mir, Masoud Salavati-Niasari, *Sol. Energ.* **86**, 3397 (2012).
9. K. Madhusudan Reddy, S.V. Manorama, A. Ramachandra Reddy, *Mat. Chem. Phys.* **78**, 239 (2003).
10. Giusepe Calogero, Gaetano Di Marco, *Sol. Energ. Mat. Sol. C* **92**, 1341 (2008).
11. S. Bégin-Colin, A. Gadalla, G. Le Caër, O. Humbert, F. Thomas, O. Barres, F. Villièras, L.F. Thomas, G. Bertrand, O. Zahraa, M. Gallart, B. Hönerlage, P. Gilliot, *J. Phys. Chem. C* **113**, 16589 (2009).
12. Soumya Sasmal, Vaibhav V. Goud, Kaustubha Mohanty, *J. Biombioe* **45**, 212 (2012).
13. Muneer M. Ba-Abbad, Abdul Amir H. Kadhum, Abu Bakar Mohamad, Mohd S. Takriff, Kamaruzzaman Sopian, *Int. J. Elecrochem. Sci.* **7**, 4871 (2012).