Indian Journal of Chemical Technology
Vol. 25, July 2018, pp. 383-389

Microwave assisted green synthesis of ZnO nanorods for dye sensitized solar cell application

P Naresh Kumar*[,1] K Sakthivel [2], V Balasubramanian[1], D Sengottaiyan[1] & J Suresh[1]

[1] Department of Physics, SNS College of Technology, Coimbatore, Tamilnadu, India.
[2]Department of Physics, Coimbatore Institute of Technology, Coimbatore, Tamilnadu, India.
E-mail: naresh_pnk@yahoo.co.in

Received 24 August 2016; accepted 28 December 2016

The rod shaped ZnO nanoparticles have been synthesized for the first time in a biological process using *Colocasia esculenta* tuber extract. Moreover, the synthesized nanoparticles have been exposed to microwave irradiation followed by annealing at 400°C. Subsequently, the FESEM and TEM images shows rod shaped morphology of synthesized ZnO nanoparticles. In addition the XRD studies reveal that the prepared ZnO nanoparticles exhibit wurtzite phase with average particle size of 13.4 nm. The Tauc plot drawn with UV-Vis spectroscopy data confirms the band gap energy of green synthesized ZnO nanoparticles as 3.12 eV. The synthesized nanoparticle is used as a photoanode in dye sensitized solar cell for the first time. The photoanodes is sensitized using natural dyes prepared from the fruit extract of *Terminalia catappa*, flower extracts of *Callistemon citrinus* and leaf extracts of *Euphorbia pulcherrima* and solar cell was fabricated. Its efficiency is found to be in the range of 1.29% to 1.60%.

Keywords: Green synthesis, Colocasia esculenta tubers, ZnO nanoparticles, Dye sensitized solar cell, Natural dyes, XRD

ZnO is a wide band gap semiconductor of the II-VI semiconductor group. It is an n-type semiconductor with band gap energy of 3.37eV[1]. The ZnO nanoparticles have remarkable properties like good photo catalyst[2], high electron mobility[3] and strong room temperature luminescence[4]. These properties enables the semiconductor to be used in various electronic applications like solar cells, sensors, memory devices, UV-light emitting diodes, piezoelectric devices, photo diodes and photo detectors. ZnO nanoparticles also possess the potential to be used as photoelectrode for energy conversion in Dye sensitized solar cells. The dye sensitized solar cells are now becoming low cost and most efficient third generation solar cell. Remarkable conversion efficiencies have been reported with ZnO nanoparticles as photoelectrodes using different nanostructures and combinations[5-7]. In spite of these achievements cost and eco-friendly nature of these cells could be improved if the natural products are involved in construction of these cells. Cost effective eco-friendly dyes and electrolyte have been utilized in these solar cells and were successful with better conversion efficiencies[8-13]. This paper projects still more greener approach to fabricate dye sensitized solar cells via biosynthesis of photoelectrode material.

These ZnO nanoparticles are produced in variety of methods like wet chemical method[14], solvothermal method[15], physical vapour deposition[16], and precipitation method[17] and spray pyrolysis method[18]. Different morphologies are indeed reported with different methods involved in the process. These methods always involve toxic reagents, expensive equipments with tedious and also time consuming process. Thus it is inevitable to prove a simple, rapid and eco-friendly method which is required to synthesize ZnO nanoparticles.

The biological methods such as the use of plant extracts, micro organisms like fungi, virus, bacteria etc. in the synthesizing nanoparticles are considered as most reliable one[19-22]. Use of these plant extracts instead of micro organisms in nanoparticle synthesis is considered to be the simple and the rapid process. The plant extracts acts as a reducing and capping agent in the synthesis process, further it also acts as a template which modifies the shape and size of the nanoparticles[23]. Different morphologies like spherical shaped silver nanoparticles[24], nanowires shaped ZnS nanoparticles[25], hexagonal shaped ZnO nanoparticles[26] and triangular shaped gold nanoparticles[27] is synthesized in biological process. Owing to the above said, literatures also illustrates that the plant extract mediated synthesis of nanoparticles are the reliable and eco-friendly method when compared to the chemical route.

In this study we report a novel synthesis of ZnO nanorods using *Colocasia esculenta* tubers extracts. The starch content in the tubers varies from 73-76%[28] which acts as a reducing agent in synthesizing ZnO nanoparticles. The synthesized nanoparticles are dried by microwave irradiation, which provides rapid and homogenous heating of the reaction mixture. The starch present in the *Colocasia esculenta* tuber extracts encapsulates the nanoparticles and shows vibration response to the microwave irradiation. Hence morphology of the nanoparticles is modified. The photoanodes for dye sensitized solar cells can be prepared by various methods like electrophoresis deposition, screen printing, doctor blade method and colloidal spray coating methods[29-32]. Among the above said methods doctor blade method is simplest and hence the photoanodes for dye sensitized solar cells were prepared by coating a thick film of synthesized ZnO nanoparticles over the conductive side of Fluorine doped Tin oxide(FTO) substrate by doctor blade method. The thick film provides more dye absorption over the nanoparticles and results in good photon to electron conversion efficiency[33]. The prepared photo electrodes is sensitized using natural dyes extracted from fruits of *Terminalia catappa*, flowers of *Callistemon citrinus* and leaves of *Euphorbia pulcherrima.* The characteristics of synthesized ZnO nanoparticles and fabricated dye sensitized solar cells is thus studied and analyzed.

Experimental Section

Precursor Zinc acetate dehydrate $Zn(CH_3COO)_2.2H_2O$ (99%), was purchased from Sigma-Aldrich. Fresh *Colocasia esculenta* tubers were purchased from local market in Coimbatore, Tamilnadu, India.

Preparation of tuber extract

The process involve cleansing, in which Fresh *Colocasia esculenta* tubers were washed thoroughly with double distilled water. The outer skin of the tubers was peeled out and the corm alone was chopped into tiny pieces. 10 g of chopped tubers were taken in a glass beaker with 200 mL of double distilled water and heated at 70°C for 30 min. Then the content was allowed to cool at room temperature, filtered and stored in a glass beaker.

Preparation of ZnO nanoparticles

The preparation of ZnO nanoparticles involve 0.2M of Zinc acetate dihydrate which was dissolved in 100 mL of de-ionized water using magnetic stirrer at 70°C for 30 min. Then 20 mL of prepared *Colocasia esculenta* tuber extract was added to the zinc acetate dihydrate solution and is stirred at 80°C for 1 hr resulting in the formation of pale white precipitate. The solution was decanted and the precipitate and is dried in microwave oven for 5 min. Finally a white powder was obtained and was annealed at 400°C for 1 hr.

Preparation of ZnO photoanodes

The ZnO photoanode was prepared by doctor blade method using a glass rod. A few drops of very dilute acetic acid were added to 1 g of synthesized ZnO nanoparticle and grinded in a mortar and pestle until a colloidal suspension with a smooth consistency was observed. Then few drops of the ZnO colloidal suspension were dropped on the conductive side of FTO substrate and spread out evenly on the surface of the FTO with glass rod. Then the substrate was dried at 200°C for 30 min and naturally cooled down to room temperature.

Extraction of natural dye sensitizers

The dyes used to sensitize the ZnO photoanode was extracted from fruits of *Terminalia catappa*, flowers of *Callistemon citrinus* and leaves of *Euphorbia pulcherrima.* The flesh from the fruits of Terminalia catappa along with the skin, flower of *Colocasia esculenta* and red leaves of *Euphorbia pulcherrima* was separately dried in shade for 15 days. The dried contents were powdered individually in a blender. Three natural dyes were prepared by soaking the powder in 100 mL of ethanol at room temperature for 24 hr in three glass beakers. Then the solid residues in each extracts were filtered out and are washed with hexane several times to remove the oil presence. The final products was stored in an amber vial and stored in refrigerator for sensitization purpose.

Sensitization of ZnO photoanode

The prepared photoanode was to be sensitized by a light absorbing dye in order to transfer electrons to the electrode by photo excitation process. Each prepared ZnO photoanode were placed into the separate beakers containing the dye extracted from the fruits of *Terminalia catappa*, flowers of *Callistemon citrinus* and leaves of *Euphorbia pulcherrima.* The sensitization process was carried in a dark environment at room temperature for about 10 hr. After sensitization the electrodes were rinsed with ethanol to remove the excess dye present in the electrode and then the electrode was dried. Thus the prepared ZnO photo electrode was sensitized with natural dyes.

Dye sensitized solar cell assembly

The dye sensitized solar cell involved basic components like dye sensitized photoelectrode (working electrode), electrolyte and a counter electrode. In this work, the dye sensitized ZnO photoanode was used as the working electrode. The platinum coated FTO glass was used as the counter electrode and placed on the top of the dye sensitized

ZnO photoanode and sealed with 30 mm thick thermal adhesive film. The Iodide/Triiodide Redox electrolyte solution was filled into the space between the photoanode and the counter electrode through a hole made on the counter electrode due to capillary action. After filling the electrolyte, the hole was sealed using the adhesive film. Thus the dye sensitized solar cell was fabricated.

Characterization

The crystalline property of the prepared ZnO nanoparticles was studied using X-ray diffractometer (Rigaku Rint 200 series). The surface morphology and chemical composition was studied using field emission scanning electron microscope and Energy Dispersive X-ray analysis respectively (SIGMA HV – Carl Zeiss with Bruker Quantax 200 – Z10 EDS Detector). The atomic structure of the sample was studied using high-resolution transmission electron microscope (JEOL, JEM-2100 microscope). The absorbance spectrum of the nanoparticles and the dye was recorded using spectrophotometer (Jasco V-570). The J-V curves of DSSCs were taken using Keithley 2400 digital source meter under an irradiation of $100 mW/cm^2$.

Results and Discussions

The X-ray diffraction patterns of the synthesized ZnO nanoparticles are shown in the Fig.1a The peaks at 31.89°, 34.46°, 36.30°, 47.55°, 56.93°, 62.93°, 66.75°, 68.15°, 77.35° corresponding to (100), (002), (101), (102), (110), (103), (201), (112), (202) positions clearly indicate the prepared sample is in wurtzite phase. No other peak related to impurities has been observed in the diffraction pattern. The particle size of synthesized ZnO nanoparticles is calculated using Debye scherrer's equation

$$D = 0.9\lambda / (\beta \cos\theta)$$

where D is the crystallite size, λ is the wavelength of X-ray used, θ is Bragg's angle and β is the full width half maximum. The average crystallite size was determined to be 13.4 nm.

Figure 1(b) shows the UV-V is absorption spectra of green synthesized ZnO nanoparticles. The absorption peak is observed at 374 nm. Fig. 1(c) shows the Tauc's plot to determine the direct band gap, the graph is plotted using $(\alpha h\nu)^2$ versus photon energy ($h\nu$). The linear portion of the graph shows the value of band gap as 3.13 eV, which is lower than the pure ZnO (3.3 eV). This reduced band gap energy may be due to some plant chemicals which are substituted in to lattice. This is in agreement with the previous studies on green synthesis of ZnO

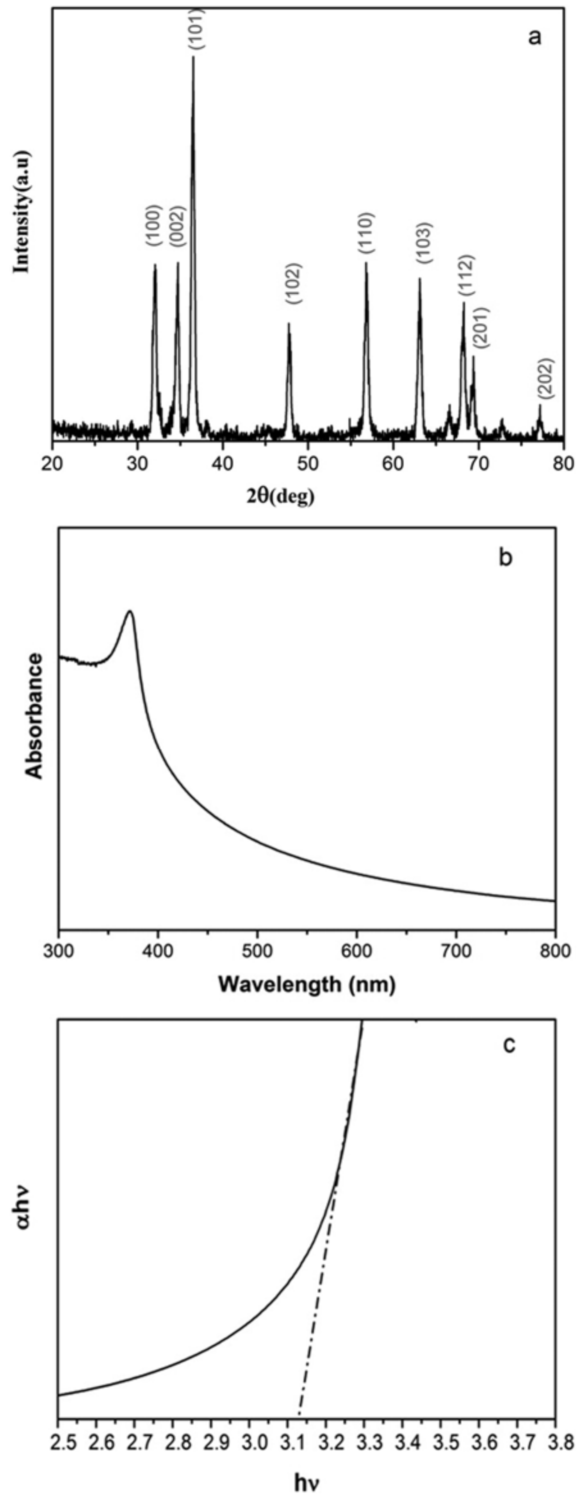

Fig 1. (a) — XRD pattern of green synthesized ZnO nanoparticles; (b) UV-Vis spectroscopy of biosynthesized ZnO nanoparticles; (c) Tauc plot of biosynthesized ZnO nanoparticles.

nanoparticles using brown marine macroalga sargassum muticum aqueous extract[34].

Figure 2(a) shows the FESEM image of green synthesized ZnO nanoparticles. The ZnO nanoparticles are in the form of nanorods with average length 179 nm and width 63 nm. Figure 2(b) shows the EDAX peaks of green synthesized ZnO nanoparticles having peaks for zinc and oxygen which confirmed the only presence of elemental Zinc and oxygen. The weight percentage of elemental Zinc and oxygen was found to be 71.23 and 28.77% respectively.

The TEM images of green synthesized ZnO nanoparticles are shown in Fig. 3 (a), (b), (c) of different magnifications. The image 3(b) and 3(c) confirms the rod shaped morphology of the synthesized ZnO nanoparticles. The selected area electron diffraction (SAED) pattern of biosynthesized ZnO nanoparticles is shown in Fig. 4(a). The pattern shows a regular polycrystalline rings with diffraction spots produced on the rings due to superposition of several single crystal orientations. The image also shows some weak diffraction spots. Figure 4(b) shows the HRTEM image of biosynthesized ZnO nanoparticles. The image shows the presence of lattice fringes with d-spacing of 2.7 Å.

Figure 5(a) shows the absorption spectra of ZnO photoanode sensitized by fruit extracts of *Terminalia catappa.* It is evident from the spectra that the sensitized photoanode absorbs a wide wavelength ranging between 420 nm to 660 nm with absorption peak at 423 nm. The light absorbance is high with *Terminalia catappa* sensitizer compared with dyes extracted from flowers of callistemon citrinus and leaves of Euphorbia pulcherrima. The light absorbance is mainly due to the compounds like β-carotene present in fruit extracts of *Terminalia catappa*. The 100 g of the fruits extracts of *Terminalia catappa* contains 2.1 mg of β-carotene which gives the bright red colour to the fruit, 138.6 mg of ascorbic acid and 7.25 mg of vitamin E as the major constituents[31].

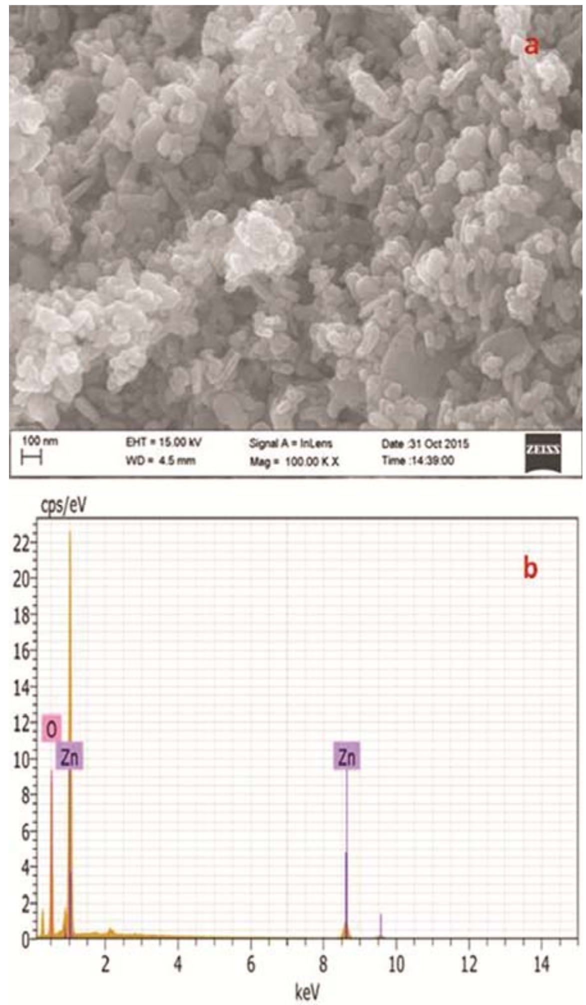

Fig. 2 (a) — FESEM image of green synthesized ZnO nanoparticles (b) EDAX peaks of green synthesized ZnO nanoparticles.

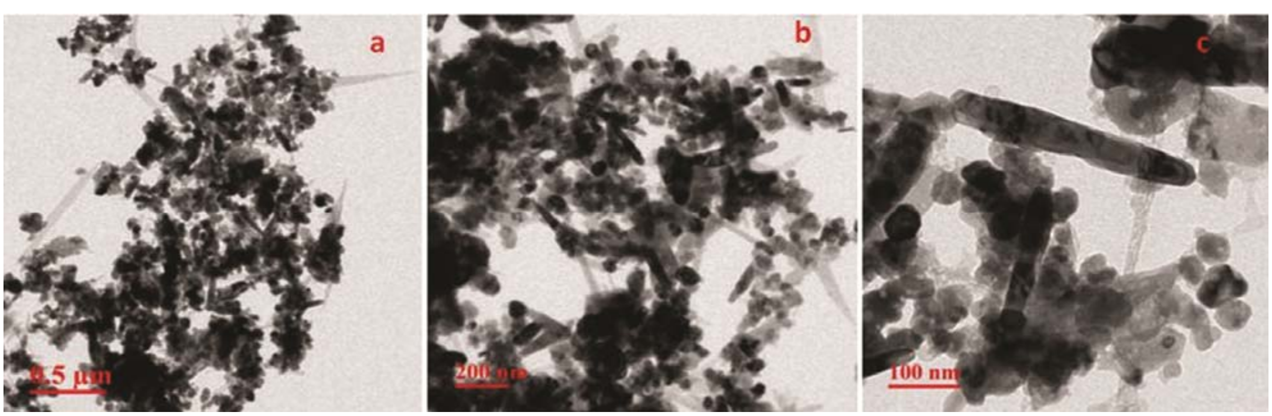

Fig. 3 — TEM images of green synthesized ZnO nanorods at various magnifications

Figure 5(b) shows the absorption spectra of ZnO photoanode sensitized with dye extracts from leaves *Euphorbia pulcherrima.* The absorption peak lies in the wavelength range between 510 nm to 580 nm which absorbs the most of the radiations from the solar spectrum. The absorbance of light is mainly due to the compound called germanicol which is present in abundant in the leaves of *Euphorbia pulcherrima.* This compound is mainly used in preparing sunscreen lotion for UV protection. The red colour of the dye is due to the presence of phytochemicals like β-amyrin and pseudotaraxasterol present in the *Euphorbia pulcherrima* leaves

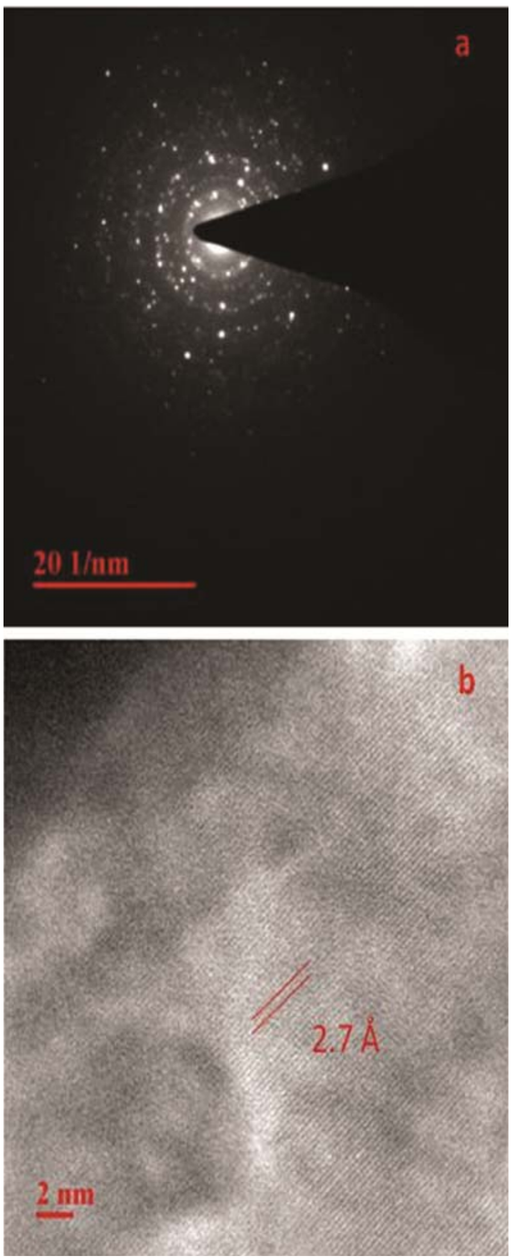

Fig. 4 — (a) SAED pattern of green synthesized ZnO nanoparticles (b) HRTEM image of biosynthesized ZnO nanoparticles.

The absorption spectra of ZnO photoanode sensitized with flower extract of *Callistemon citrinus* is shown in Fig. 5(c). The absorption spectra shows low absorbance compared with the other two dyes. No sharp peak was observed over this dye but the absorbance was noticed in the wavelength range between 400 nm to 650 nm. The flower extracts of *Callistemon citrinus* contains cyanidin-3, 5-diglucoside which provide red colour to the flower.

Figure 6 shows the J-V characteristics of prepared solar cells. The current density for the voltage developed were recorded and plotted in graph. The solar cell parameters like open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), and efficiency (η) is calculated from the plotted graph using the formula

$$FF = \frac{jmax\ X\ Vmax}{jsc\ X\ Voc}$$

$$Efficiency = \frac{Jsc\ X\ Voc\ X\ FF}{Pin}$$

The dye sensitized solar cells fabricated with ZnO photoanodes sensitized with fruit extracts of *Terminalia catappa* shows 1.60% of efficiency whereas with leaf extracts of *Euphorbia pulcherrima* and flower extracts of *Callistemon citrinus* show 1.29 and 1.33% respectively. The higher efficiency in solar cell sensitized with *Terminalia catappa* dye is due to high light absorbance over a wide range of spectrum.

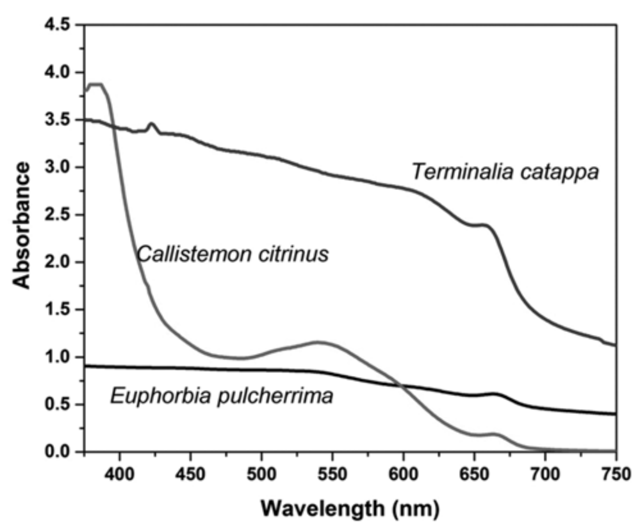

Fig. 5 — Absorbance spectra of ZnO photoanode sensitized by fruit extracts of *Terminalia catappa*, leaf extracts of *Euphorbia pulcherrima* and flower extracts of *Callistemon citrinus*.

The devices remained stable for 15 day after which there was a decrease in J_{sc} values

The result substantiates that the natural dye can be used as an effective sensitizer with some modification in morphology of photoanode. The rod shaped nanoparticles absorbs good amount of dye on its surface due to green synthesis process involved. The ZnO nanoparticles also have some organic compounds attached to its surface, which binds the dye to its surface. The results show the green synthesized nanoparticles could improve the efficiency of dye sensitized solar when sensitized with natural dyes.

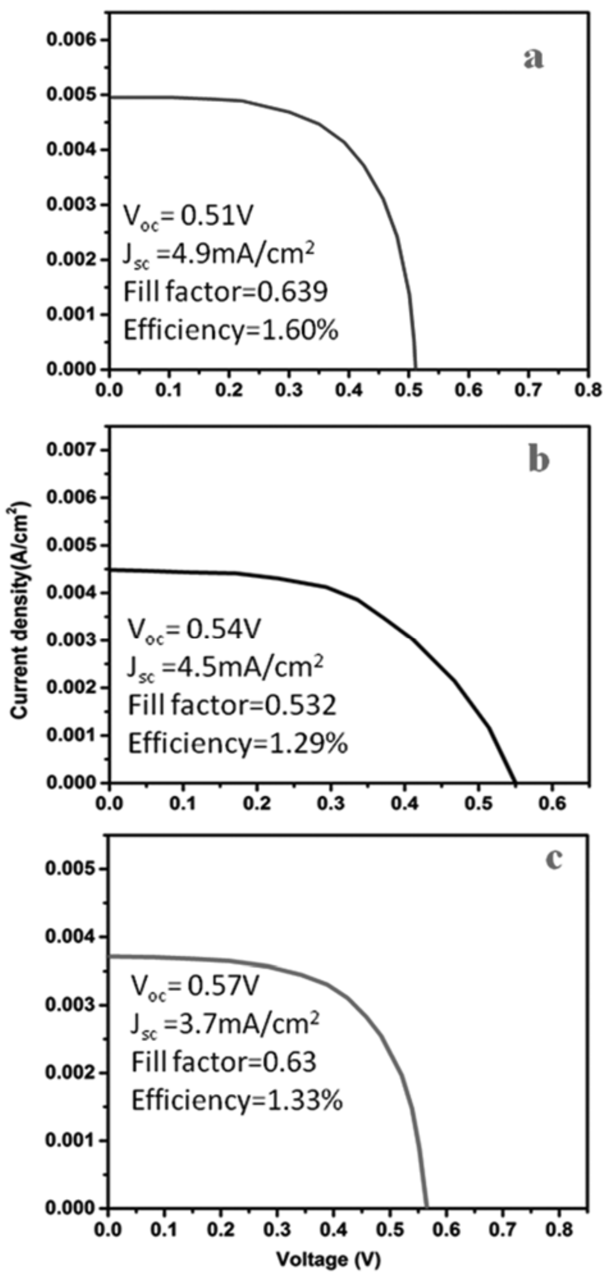

Fig. 6 — J-V characteristics of biosynthesized ZnO based solar cells sensitized by (a) natural dyes extracted from fruits of *Terminalia catappa*, (b) leaves of *Euphorbia* pulcherrima and (c) flowers of C*allistemon citrinus.*

Conclusion

The rod shaped ZnO nanoparticles have been synthesized by microwave assisted green synthesis method for the first time. The rod shaped morphology is obtained due to the phytochemicals present in *Colocasia esculenta* tuber extracts. The X-ray diffraction studies and EDAX spectrum confirms the prepared sample is ZnO nanoparticles. The band gap energy determined from UV-Vis spectroscopy studies is 3.13 eV. The prepared ZnO nanoparticle is used as photoanodes in dye sensitized solar cell. The prepared photoanode is sensitized using natural dyes extracted from fruits of *Terminalia catappa*, flowers of C*allistemon citrinus* and leaves of *Euphorbia pulcherrima* and their photo electrochemical properties were analyzed. Thus the solar cell fabricated using ZnO sensitized with fruits of *Terminalia catappa* exhibited a better efficiency of 1.60%.

References

1 Nasiri N, Bo R, Hung T F, Roy V A L, Fu L & Tricoli A, *Adv Funct Mater*, 26 (2016) 7359.
2 Fan J, Li T & Heng H B, *Mater Sci*, 39 (2016) 19.
3 Ka Y, Jang H R & Choi W S, *Sci Adv Mater*, 8 (2016) 382.
4 Huang C Y & Lai J H, *Org Electron,* 32 (2016) 244.
5 Çakar S & Özacar M, *Spectrochim Acta A*, 163 (2016) 79.
6 Ali N, Hussain A, Ahmed R, Wang M K, Zhao C, Haq B U & Fu Y Q, *J Renew Sustain Ener*, 59 (2016) 726.
7 Gopi C V V M, Venkata-Haritha M, Lee Y S & Kim H J, *J Mater Chem* A, 4 (2016) 8161.
8 Hug H, Bader M, Mair P & Glatzel T, *Appl Energ,* 115 (2014) 216.
9 Li S, Liu W, Shi M, Mai J, Lau T K, Wan J, Lu X, Li C Z & Chen H, *Energ Environ Sci*, 9 (2016) 604.
10 Chiappone A, Bella F, Nair J R, Meligrana G, Bongiovanni R & Gerbaldi C, *Chemelectrochem,* 1 (2014) 1350.
11 El-Ghamri H S, El-Agez T M, Taya S A, Abdel-Latif M S & Batniji A Y, *Mater Sci Poland*, 32 (2014) 547.
12 Kumar P N & Sakthivel K, *J Ovonic Res,* 11 (2015) 169.
13 Vanalakar S A, Patil V L, Harale N S, Vhanalakar S A, Gang M G, Kim J Y, Patil, P S & Kim J H, *Sensor Actuat B-Chem*, 221 (2015) 1195.
14 Liu X, Chen N, Xing X, Li Y, Xiao X, Wang Y & Djerdj I, *Rsc Adv,* 5 (2015) 54372.
15 Garc'ia-Gutiérrez R, Barboza-Flores M, Berman-Mendoza D, Rangel-Segura R & Contreras-López O E, *Adv Mater Sci Eng*, 2012.
16 Raoufi, D, *Renew Energ,* 50 (2013) 932.
17 Sivalingam K, Shankar P, Mani G K & Rayappan J B B, *Mater Lett*, 134 (2014) 47.

18 Thema F T, Beukes P, Gurib-Fakim, A & Maaza M, *J Alloy Compd*, 646 (2015) 1043.

19 Raliya R, Tarafdar J C & Biswas P, *J Agr Food Chem*, 64 (2016) 3111.

20 Love A J, Makarov V V, Sinitsyna O V, Shaw J, Yaminsky I V, Kalinina N O & Taliansky M E, *Front Plant Sci,* 6 (2015).

21 Salunke B K, Sawant S S, Lee S I & Kim B S, *Appl Microbiol Biot*, 99 (2015) 5419.

22 Rauwel P , Küünal S, Ferdov S & Rauwel E, *Adv Mater Sci Eng*, 2015.

23 Vigneshwaran N, Ashtaputre N M, Varadarajan P V, Nachane R P, Paralikar K M & Balasubramanya R H, *Mater Lett,* 61 (2007) 1413.

24 Mao C, Flynn C E, Hayhurst A, Sweeney R, Qi J, Georgiou G, Iverson B & Belcher A M, *P P Natl Acad Sci Usa*, 100 (2003) 6946.

25 Chung I M, Rahuman A A, Marimuthu S, Kirthi A V, Anbarasan K & Rajakumar G, *Nanomaterials-Basel*, 5 (2015) 1317.

26 Ghodake G S, Deshpande N G, Lee Y P & Jin E S, *Colloid Surface B*, 75 (2010) 584.

27 Prajapati R, Kalariya M, Umbarkar R, Parmar S, Sheth N, *Int J Pharmacol*, 1 (2011) 90.

28 Zarazúa I, Esparza D, López-Luke T, Ceja-Fdez A, Reyes-Gomez J, Mora-Seró I & de la Rosa E, *Electrochim Acta*, 188 (2016) 710.

29 Schmidt I, Plettenberg I, Kimmich D, Ellis H, Witt J, Dosche C & Wittstock G, *Electrochim Acta,* (2016).

30 Hosseini Z, Taghavinia N & Diau E W G, *Mater Lett* (2016).

31 Susmitha K, Kumari M M, Berkmans A J, Kumar M N, Giribabu L, Manorama S V & Raghavender M, *Sol Energy,* 133 (2016) 524.

32 Yang W G, Wan F R, Chen Q W, Li J J & Xu D S, *J Mater Chem* A, 20 (2010), 2870.

33 Azizi S, Ahmad M B, Namvar F & Mohamad R, *Mater Lett,* 116 (2014) 275.

34 Dikshit M & Samudrasok R K, *Int J Food Sci Nutr,* 62 (2011) 47.