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# Natural dye sensitized solar cell using sol gel dipcoated Zinc Oxide nanorods

J.Deenathayalan[1,*], M.Saroja[2], M.Venkatachalam[2], P.Gowthaman[2], and S.Shankar[2]

[1]Department of Electronics, Sri Vasavi College, Erode, Tamilnadu, India

[2]Department of Electronics, Erode Arts and Science College, Erode, Tamilnadu, India.

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**ABSTRACT**

Preparation of ZnO nanorod based natural dye-sensitized solar cell is reported. Seed layers were deposited on glass / ITO substrates using dip coating method with zinc acetate dihydrate as starting material. ZnO nanorods were fabricated on induced seeds by hydrothermal method using hexamethylenetetramine as a precipitant and zinc nitrate as source at 90°C. The crystal structure, orientation and surface morphology were investigated by X-Ray diffractometer and Scanning Electron Microscopy. Optical properties were studied using UV-visible spectroscopy. Prepared ZnO nanorods were employed as wide band gap semiconductor to construct natural dye-sensitized solar cells. Various natural dyes, extracted from natural plants such as leaves and flowers were used as sensitizers for natural dye-sensitized solar cells. The fill factor and solar-light-to-electricity conversion efficiency were obtained.



## Introduction

ZnO is a widely used versatile functional material with wide and direct band gap, large excitation binding energy and excellent chemical and thermal stability material from which zinc oxide nanostructures such as nano tubes [1], nano wires [2], nanorods [3], nano belts [4], nano cables and nano ribbons [5] stimulate considerable interests for scientific research due to their importance in fundamental physics studies. Several methods for the synthesis of nano structured ZnO have been explored, but some of them are highly power demanding [6], or they use sophisticated processes to obtain the materials by means of a vapor-liquid-solid mechanisms [7-9], that makes the scaling up a complicated challenge [10].

One of the most promising methods to synthesize nanorods is the hydrothermal method, which is low-temperature and low cost method [11-13]. Additionally, the above method has a high degree of versatility to modify several parameters, such as temperature, pH [14] and concentration of reactants, which in turn could modify the morphology, size and shape of the nanorods [15]. Dye Sensitized Solar Cells (DSSCs) have the potential to convert solar power to electricity efficiently and at a low cost, making it promising solar cell architecture for large scale solar energy implementation.

## Experimental

ZnO nanorods were grown on glass / ITO substrates via a two-step process. In the first step, a thin seed layer was prepared on glass / ITO substrates by sol-gel technology. In the second step, ZnO nano rods were grown on seed layer coated glass / ITO substrates by hydrothermal technique.

### *Preparation of ZnO seed layers*

0.22 gram of zinc acetate powder and 10 ml of ethanol was mixed and 0.25 ml of de-ionized water was added drop by drop through syringe to the above solution. This solution was stirred continuously for 2 hours at room temperature for obtaining clear homogenous solution. The stirred solution was taken in a beaker and the well cleaned glass / ITO substrates were dipped in the solution for five times at regular intervals at room temperature using automatic dip coating system (Holmarc - HO-TH-02). Then this five layer films were annealed in a furnace at a temperature of 200°C for 1 hour.

### *Preparation of ZnO nanorods*

Hydrothermal method was carried out by suspending the ZnO seed coated glass / ITO substrates. ZnO nanorods were grown using hydrothermal method by immersing a seeded glass / ITO substrate in a glass beaker to containing 0.02 mol of zinc nitrate and 0.2 mol of hexamethylenetetramine (HMT) solution on 1:10 molar concentration, which is the optimized ratio to grow ZnO nano rods, as reported in our prior work [16]. The solution was heated in a hot air oven and maintained at 90°C for 4 hours. At the end of the growth period, the substrates were removed from the solution and rinsed immediately with deionized water to remove the residuals from the surface and dried in air at room temperature. Then the above films were annealed in muffle furnace at different temperatures of 300°C, 400°C and 500°C for 1 hour.

### *Preparation of natural dye sensitized solar cell*

In the preparation of DSSC, selection of natural dyes plays an important role. [17]. In the present work, three types of natural plants were selected for extraction of dyes; they are morus alba leaves, amaranthus cacdadus leaves and albizia lebbeck flowers. The leaves and flowers were first cleaned with de-ionized water and dried in the air atmosphere. The dried plants were made into pieces and immersed in ethanol solution for 24 hours. After filtration, the solutions of the natural dyes were obtained. The prepared natural dyes of morus alba, amaranthus cacdadus and albizia lebbeck were diffused into the prepared ZnO nanorods. The natural dyes were taken in a beaker and the ZnO nanorod coated ITO substrates were immersed in the dye solution. After 24 hours the substrates were taken out and dried in the hot air oven at 70°C for 30 minutes. The prepared dye diffused ITO substrates were used as working electrodes for dye sensitized solar cell.

Tele:

E-mail addresses: jd10173@gmail.com

The carbon counter electrode was fabricated by exposing the ITO substrates to the carbon flames from a candle. The carbon deposited counter electrode was placed on the top of the natural dye sensitized ZnO electrode and the two electrodes were clamped firmly together with the binder clip and this resulted in a sandwich-type cell. The electrolyte was prepared using iodine, lithium iodide and acetonitrile. This mixture was used as a redox couple to improve the properties of the electrolyte and the operating performance of the DSSC.

The X-ray diffraction pattern of the prepared ZnO samples was recorded using a XPERT-PRO with Cu Kα radiation at the Bragg angle ranging from 20° to 80°. The surface morphology of the prepared samples has been studied using scanning electron microscope SEM JEOL-6390. The absorbance spectra have been recorded using a spectrophotometer JASCO V-570. The I-V characteristics of the devices in the dark and under illumination were measured by semiconductor parameter analyzer (Keithley 4200-SCS). A Xenon light source (Philips) was used to give an irradiance of 100 mW/cm$^2$.

**Results And Discussion**

The crystal structure of samples annealed at different temperatures of 300 °C, 400 °C, 500 °C and as prepared sample was analyzed by XRD and shown in fig 1. All diffraction peaks are well indexed to the standard diffraction pattern of hexagonal wurtzite ZnO phase. The detected (h k l) peaks were at 2θ values of 31.7647°, 34.4227° and 36.2520° corresponding to the lattice planes (100), (002) and (101) respectively. The strong and narrow diffraction peaks indicate that the material has a fine crystallinity. The XRD pattern of as prepared film shows that, it has all the three peaks with small and equal intensity, indicating the nanorods were grown in all directions. The XRD pattern of film annealed at 300°C has a weak (101) peak and weak (100) peak and moderate (002) peak. At 400°C the (101) and (100) peaks were suppressed and (002) peak is increased. The XRD pattern of film annealed at 500°C has a very strong (002) peak, very weak (100) and (101) peaks as reported in our prior work [18].

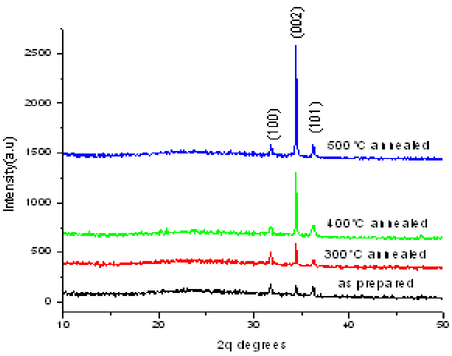


**Fig.1 XRD spectra of ZnO nanorod at different annealing temperatures**

From the above XRD patterns it is clearly seen that, as the annealing temperature increases the diffraction peaks were oriented strongly along the (002) peak. This implies that the grown nanorods confirm c-axis point of reference. The XRD pattern of as prepared film shows that the peaks are oriented in all directions along the ZnO structure. It implies that the annealing temperature influences the orientation, crystalline nature of the ZnO nanorods. The average size of the ZnO particle is calculated using Debye scherer formula, davg = 0.9λ / β Cosθ. Where davg = average crystal size, λ= wavelength of incident beam (1.5406Å), β= FWHM in radians, θ= scattering angle in degree. The grain size of the nano particles are found to be 1.12nm, 1.62nm, 2.80nm and 2.03nm for annealing temperatures of 300 °C, 400°C, 500°C and as prepared ZnO nano rods.

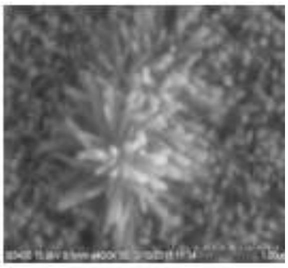

***Fig. 2(a)***

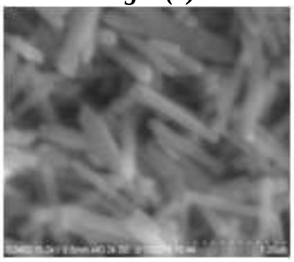

***Fig. 2(b)***

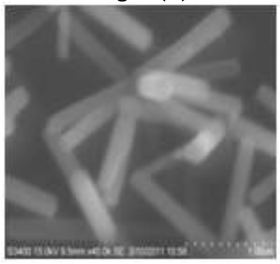

***Fig. 2(c)***

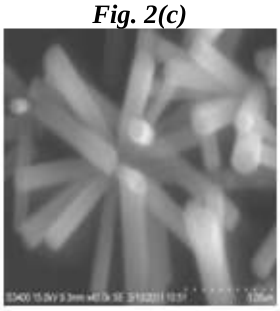

**Fig. 2(d)**

***Fig.2 (a-d) SEM images of as prepared, 300°C, 400°C and 500°C annealed ZnO nanorods***

The SEM images of the as prepared ZnO nanorods and nanorods annealed at 300 °C, 400°C and 500°C were shown in Fig. 2 (a-d). The sizes of the ZnO nanorods were standardized and the mean size is about 100 - 300 nm. The images can be indexed as hexagonal Wurtzite-structural ZnO, which is very consistent with the analysis of XRD. It is observed from the SEM images that the diameter of the ZnO nano rods increases as the annealing temperature increases. In Fig.2a the rods grown exhibit flower like structure. In Fig.2b the rods were grown in all directions, where all three peaks of XRD pattern are quite reflected. In Fig 2c the rods were grown towards c-axis orientation as indicated in XRD pattern. In Fig.2d the grown nanorods were mostly set in vertical direction and it is similar to the XRD pattern in which (002) peak was strong. It implies that the annealing temperature strongly influences the growth of ZnO nanorods. From the XRD and SEM results, it is clearly seen that good quality ZnO nanorods can be grown at annealing temperature of 500°C.

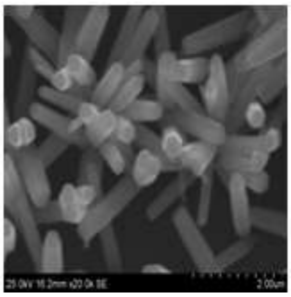

*Fig.3 SEM image of ZnO nanorods grown on ITO substrate.*

To prepare dye sensitized solar cell, the ZnO nanorods were grown on ITO substrate. The SEM image of the ZnO nanorods grown on ITO substrate and annealed at 500°C is shown in Fig. 3. The nanorods grown on ITO substrate exhibit better c-axis orientation.

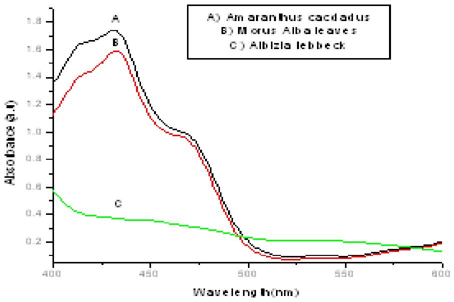


**Fig.4.UV – Vis absorption spectra of different dye solutions.**

Fig. 4 shows the UV–Vis absorption spectra of amaranthus cacdadus, morus Alba and albizia lebbeck extracts. It was found that the absorption peaks of amaranthus cacdadus and morus alba extracts were 435 nm and 430 nm respectively. In the case of albizia lebbeck extract no absorption peak was found. The variation in the absorption characteristics is due to the different type of anthocyanins and colors of the extracts.

The ZnO nanorod coated ITO substrates were immersed in the dye extracts and were used as working electrodes in DSSC. The absorption spectra of the working electrodes are shown in Fig. 5. In the case of amaranthus cacdadus and morus alba extracts adsorbed on ZnO, the absorption peaks were higher than that of the pure ZnO nano rods. The difference in the absorption peak is due to the binding of the extract to the oxide surface. In the case of albizia lebbeck extract no absorption peak was found. This is due to the loading effect of the extract into the film surface which suppressed the absorption peak.

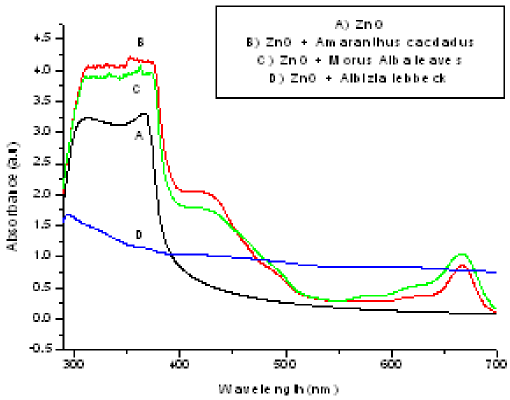


**Fig.5. UV – Vis absorption spectra of: (a) pure ZnO; (b) Amaranthus cacdadus (c) Morus Alba and (d) Albizia lebbeck extracts adsorbed on ZnO.**

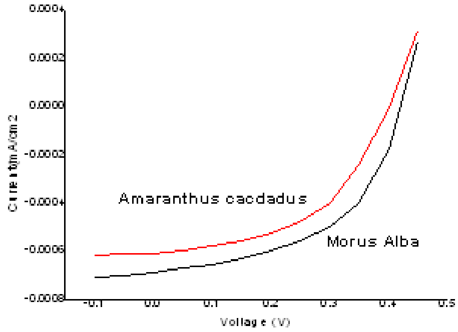


*Fig.6. I-V curves for natural DSSC from (a) Amaranthus cacdadus (b) Morus Alba leaves*

Fig.6 shows the current – voltage (I-V) characteristics for DSSCs constructed using amaranthus cacdadus and morus alba and measured under a stimulated illumination with a light intensity of 100mW / cm$^2$. The fill factor (FF) of the natural DSSC was calculated using the equation,

$$FF = I_{max} V_{max} / I_{sc} V_{sc} \quad (1)$$

and the incident photon – to – current (IPCE) efficiency (ή) was calculated using the equation

$$ή\ (\%) = I_{max} V_{max} / P_{inc} \quad (2)$$

where $I_{max}$ and $V_{max}$ are the current and voltage obtained at the maximum power point on the photovoltaic power output curve and $P_{inc}$ is the power density of the incident radiation respectively. In principle, the maximum $I_{sc}$ of a dye-sensitized solar cell is determined by how well the absorption window of the dye overlaps with the solar spectrum. The solar cell parameters are given in Table 1.

*Table 1: Solar cell parameters*

| Sensitizer | $I_{SC}$ | $V_{SC}$ | FF | ή% |
|---|---|---|---|---|
| Amaranthus cacdadus | 6.92mA / cm$^2$ | 0.419V | 0.51 | 0.30 |
| Morus alba | 6.91mA / cm$^2$ | 0.399V | 0.43 | 0.24 |

From the above results, it can be seen that the Isc and Vsc and FF for the cell constructed using amaranthus cacdadus represent clear improvement over the cell constructed using morus alba.

**Conclusion**

ZnO nanorods were synthesized by simple sol-gel dip coating method at low growth temperature of 90°C via the hydrothermal method and annealed at three different temperatures. From the results of XRD and SEM, it was clearly observed that good quality ZnO nanorods can be grown on ITO substrate at the annealing temperature of 500°C. These ZnO nanorods were used for the preparation of DSSC with natural plant extracts of amaranthus cacdadus and morus alba. Due to the improved Isc and FF, the amaranthus cacdadus based DSSC reached a total IPCE of 0.30%, outperforming that of the morus alba based DSSC.

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