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Dye-sensitized ZnO nanorod based photoelectrochemical solar cells with natural dyes extracted from Ixora coccinea, Mulberry and Beetroot

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Abstract ZnO nanorods have been prepared on indium tin oxide (ITO) glass substrates coated with sol–gel based ZnO seed layer through chemical method. Natural dyes (Ixora coccinea, Mulberry and Beetroot) have been used for the fabrication of dye sensitized solar cells. The surface morphology studied using scanning electron microscope shows that the vertically aligned ZnO nanorods are of hexagonal shape. The solar cell efficiency has been calculated and is found to be 0.33, 0.41 and 0.28% for Ixora coccinea, Mulberry and Beetroot extract dye sensitized solar cells.

1 Introduction

Recently, many efforts have been expended in controlling the size, shape, dimensionality and crystal structure of inorganic oxides such as TiO_2, SnO_2, ZnO, etc., for the improvement of opto-electrical properties. Compared to other metal oxides, the wurtzite structure of ZnO favors the formation of anisotropic structures such as nanorods, nanowires, nanotubes etc. In order to utilize the nanostructure materials for applications, it usually requires that the crystalline morphology, orientation and surface architecture of nanostructures are well controlled during the preparation processes. ZnO nanostructures such as nanowires [1], nanorods [2], nanotubes [3], nanocoral [4] and nanoflowers [5] have been used in the fabrication of dye sensitized solar cells. The chemical method is a low-cost, simple and large-scale route for growing ZnO nanostructures directly on the substrate. Hsu et al. [6] have fabricated dye sensitized solar cells using hydrothermally and vapor phase grown ZnO nanorods and have reported a conversion efficiency of 0.22%. Huimin Gao et al. [7] have grown ZnO nanorods and have used them to construct solar cell and have reported that the efficiencies are in the range 0.08–0.32%. Wu et al. [8] have fabricated mercurochrome sensitized ZnO nanowire based solar cells and have reported an efficiency of 0.83%.

Organic dyes used in the dye-sensitized solar cells often bear a resemblance to dyes found in plants, fruits, and other natural products, and several dye-sensitized solar cells with natural dyes have been reported [9–11]. Garcia et al. [10] have reported that wavelengths of maximum absorption spectra of dye coated TiO_2 electrodes are slightly red shifted compared to the corresponding dye solution spectra. The nanowire based dye sensitized solar cell have J_{sc} of 1.3 mA cm^{-2}, V_{oc} of 0.67 V, FF of 32% and an overall efficiency of 0.3% [12]. Wongcharee et al. [13] have fabricated solar cells using natural dyes extracted from rosella, blue pea and a mixture of the extracts and has reported the efficiency to lie in the range 0.57–0.33%. Ortiz et al. [14] have reported best efficiency of 0.01% for bixin sensitized ZnO cells. Latha and Panikkar have reported that Ixora coccinea flowers are extensively used in Ayurvedic

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medicine [15]. To the best of our knowledge, the Ixora coccinea, Mulberry and Beetroot have not been previously used as dye sensitizers for solar cell application. In this paper, we report about the growth of ZnO nanorods and the fabrication of dye (Ixora coccinea, Mulberry and Beetroot) sensitized ZnO nanorod based photoelectrochemical solar cells. The use of nontoxic natural pigments as sensitizers would definitely enhance the environmental and economic benefits of this alternative form of solar energy conversion.

2 Experimental

In the present study, ZnO nanorods have been prepared by a two step simple chemical method. In the first step, ZnO seed layer has been prepared using sol–gel dip coating method. Zinc acetate dihydrate $(CH_3COO)_2$ Zn.$2H_2O$) was dissolved in a mixure of ethanol and ethanolamine ($H_2NCH_2CH_2OH$) at room temperature. The resultant solution was stirred for 1 h to yield a homogeneous, clear and transparent solution using magnetic stirrer. The dip coating method has been used to prepare thin films of ZnO using the prepared sol onto ITO coated glass substrates. After deposition, annealing of the samples was carried out for the removal of solvent and residual organics and film densification. ZnO thin films of thickness 200 nm was formed. The films were post annealed at 450 °C for 1 h and these films form the ZnO seed layer. In the second step, an aqueous solution was prepared by dissolving zinc nitrate (Zn $(NO_3)_2{\cdot}6H_2O$) and hexamine ($(CH_2)_6{\cdot}N_4$) in deionized water. The concentration of zinc nitrate was 0.03 mol/L and molar concentration of zinc nitrate to hexamine was kept at 1:1. The ZnO seed-layer coated substrates were vertically dipped in the (zinc nitrate + hexamine) solution and solution was heated with a laboratory oven and maintained at 70 °C for 4 h. At the end of the growth period, the substrates were removed from the solution and were thoroughly washed with deionized water to remove the residual salt from the surface and annealed at 300 °C for 3 h. This resulted in the formation of ZnO nanorods.

Then, the dye was incorporated onto the ZnO nanorods surface by dipping the substrate into the dye solution. In this study, three kinds of dyes were used. One was the dye of Ixora coccinea, and the others were the dye of Mulberry and Beetroot. The solvent used in the preparation of Ixora coccinea, Mulberry and Beetroot dye was ethanol.

The surface morphology of the samples has been studied using FEI QUANTA 200 scanning electron microscope (SEM), the presence of the elements Zn and O have been identified using energy dispersive X-ray analysis (EDAX, Thermo-Noran system Six) and the optical properties has been studied using the absorbance spectrum recorded using spectrophotometer (JASCO V-570). A thin sandwich type photoelectrochemical solar cell has been fabricated using the dye sensitized ZnO nanorods electrode, Pt coated ITO as counter electrode, a spacer film and an electrolyte solution. 0.1 M lithium iodide and 0.03 M iodine were dissolved in acetonitrile and was used as the electrolyte solution. The dye sensitized ZnO nanorod active electrode area was typically 0.25 cm^2. The J–V characteristics of the cell was recorded using a Keithley 4200-SCS meter. A xenon lamp source (Oriel, USA) with an irradiance of 50 mW/cm^2 was used to illuminate the solar cell (equivalent to AM1.5 irradiation).

3 Results and discussion

Figure 1a is the scanning electron microscope image showing the vertically aligned ZnO nanorods. The ZnO nanorods have been grown vertically from seed layer. ZnO nanorods are observed to be hexagonal in shape with the diameter ranging from 100 to 200 nm and height of 1 μm. The SEM image of ZnO nanorods with Ixora coccinea, Mulberry, Beetroot extract are shown in Fig. 1b, c and d. Energy dispersive x-ray analysis (EDAX) of ZnO is shown in Fig. 2. EDAX spectra results show the presence of Zn, O and Au. Au peak in the spectra is due to the gold conductive coating on the substrate.

Optical absorption spectra of Ixora coccinea and Ixora coccinea extract absorbed on ZnO nanorods are shown in Fig. 3. It is observed that the dye sensitized ZnO electrodes are more photoactive in the region 400–550 nm. Optical absorption spectra of Mulberry extract and Mulberry extract absorbed ZnO nanorods are shown in Fig. 4. The absorption spectra of Mulberry dye absorbed on ZnO nanorods is shifted to longer wavelength with a maximum peak at about 560 nm compared to 535 nm of mulberry dye solution. It is well known fact that high dye absorption by thin film leads to high light harvesting efficiency. Optical absorption spectra of beetroot extract and beetroot extract absorbed on ZnO nanorods are shown in Fig. 5. It is seen (Fig. 5) that the absorption peaks of beetroot extract are at 483 and 546 nm. Sivakumar et al. [16] have reported beetroot absorption peaks corresponding to (1) Betaxanthin (yellow color) −480 nm and (2) Betanin (red color) −530 nm. Beetroot extract coated on ZnO nanorods show a strong absorption peak at 483 nm suggesting that the yellow betaxanthins compounds are more strongly absorbed than betanin.

The J–V characteristics of Ixora coccinea, Mulberry and Beetroot dye sensitized ZnO nanorods based solar cells are shown in Fig. 6. The fill factor (FF) of the solar cell fabricated has been calculated using the equation

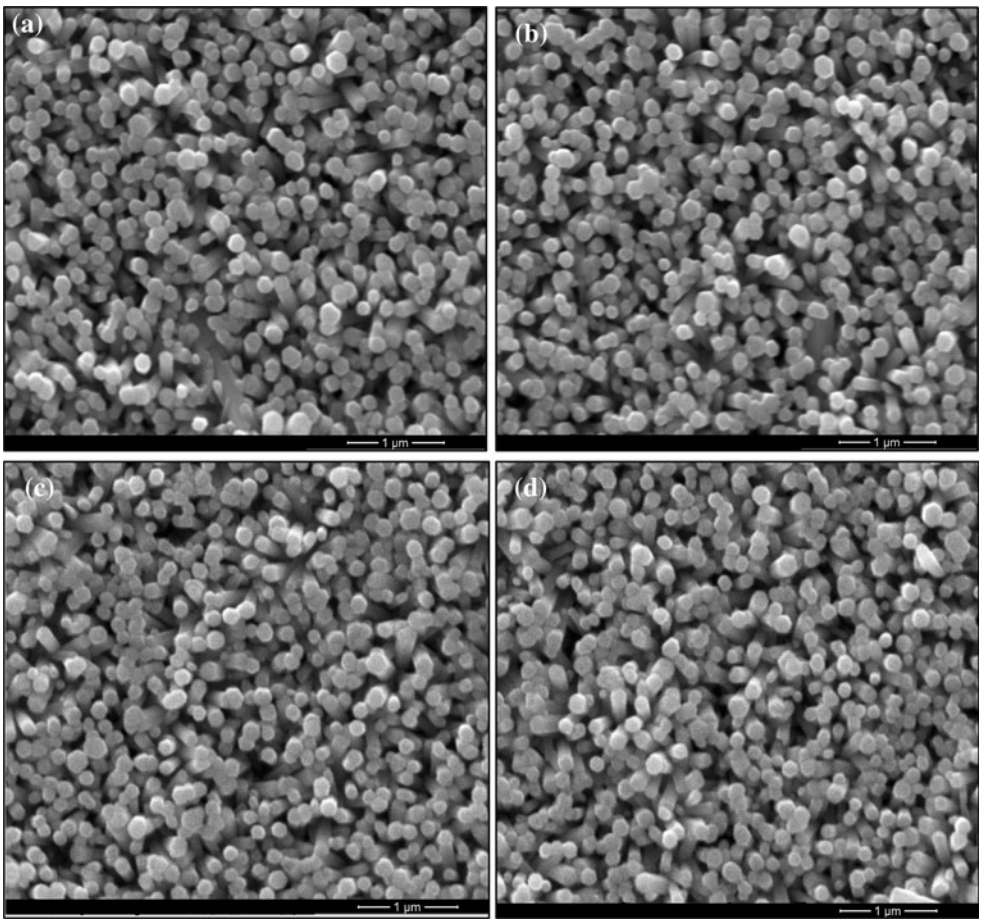

Fig. 1 SEM image of **a** ZnO nanorods, **b** Ixora coccinea sensitized ZnO nanorods **c** Mulberry sensitized ZnO nanorods and **d** Beetroot sensitized ZnO nanorods

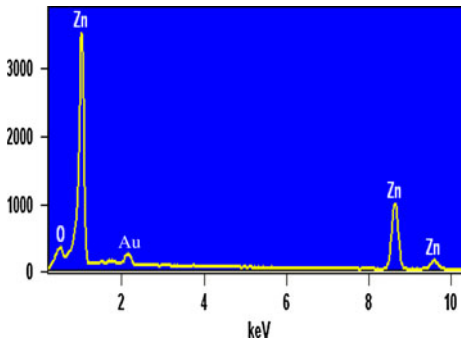

Fig. 2 EDAX spectra of ZnO

$$FF = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}} \quad (1)$$

The overall conversion efficiency (η) is expressed by the following equation

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \quad (2)$$

where P_{in} is the intensity of incident light, FF is fill factor, V_{max} and J_{max} are voltage and current density at maximum power output, and V_{oc} and J_{sc} are open circuit photovoltage and short circuit photocurrent, respectively. The η of the Ixora coccinea (Fig. 6) dye sensitized ZnO nanorod

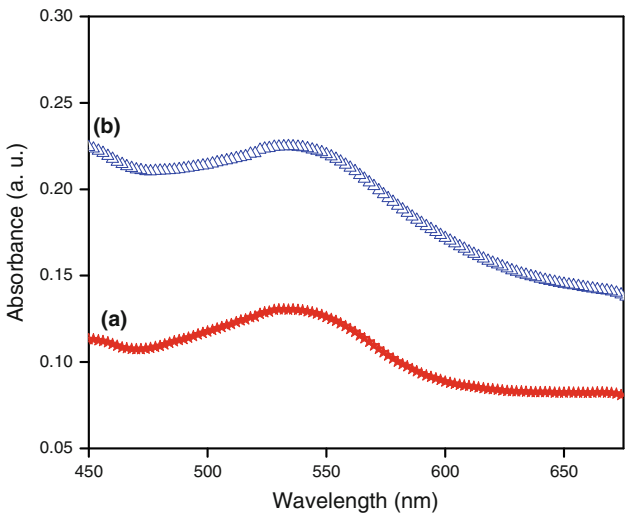

Fig. 3 Absorption spectra of **a** Ixora coccinea extract and **b** Ixora coccinea extract absorbed ZnO nanorods

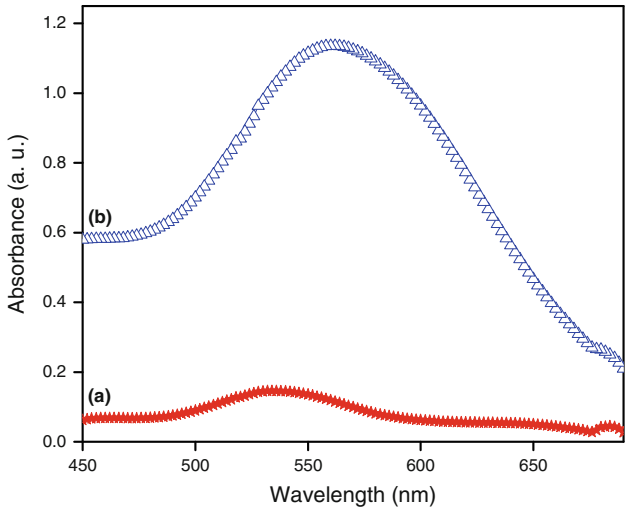

Fig. 4 Absorption spectra of **a** Mulberry extract and **b** Mulberry extract absorbed ZnO nanorods

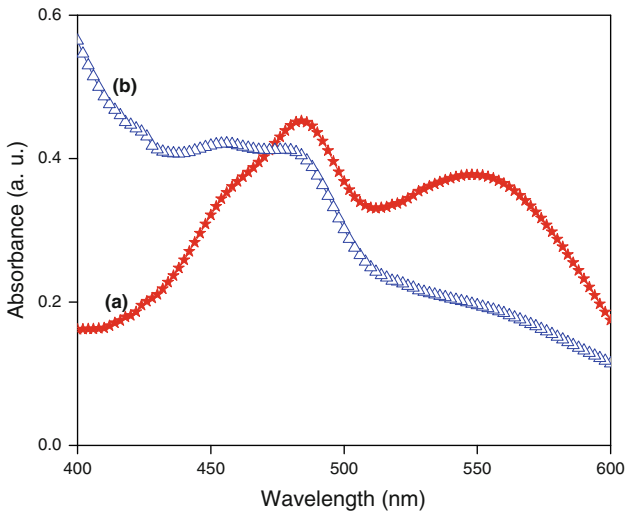

Fig. 5 Absorption spectra of **a** Beetroot extract and **b** Beetroot extract absorbed ZnO nanorods

solar cells is 0.33% with short circuit current density 2.65 mA cm^{-2}, open circuit voltage 0.21 V and fill factor 0.29%; while the η of the Mulberry (Fig. 6) dye sensitized solar cells using ZnO nanorods electrode is 0.41% with short circuit current density 2.90 mA cm^{-2}, open circuit voltage 0.23 V and fill factor 0.30. The η of the beetroot dye sensitized solar cells using ZnO nanorods electrode is 0.28% with short circuit current density 2.30 mA cm^{-2}, open circuit voltage 0.2 V and fill factor 0.30% FF. The relatively low photo current is due to the low injection yield and charge collection. The injection yield for ZnO nanorods is low either due to limited overlap of the excited state of the dye and ZnO conduction band or due to weak adsorption and interaction of the dye with the ZnO nanorod surface. The dye regeneration kinetics and dye excited state

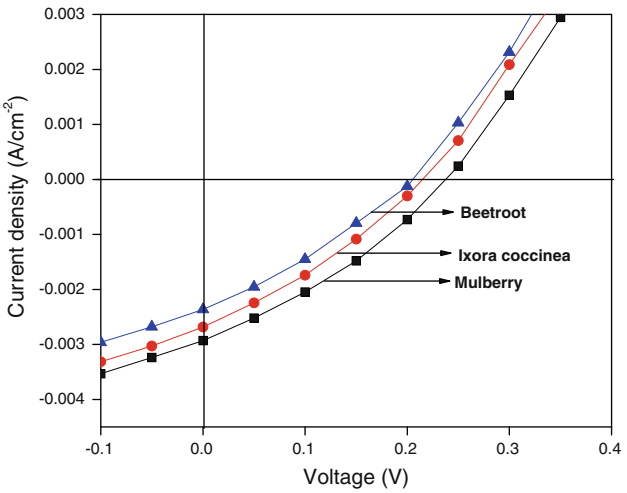

Fig. 6 J–V characteristics of dye sensitized ZnO nanorods based solar cells

life time may not be optimal. Increase of dye compound adsorption increases the absorbed light energy and the enhancement of incident light capture. The low fill factor may be attributed to the recombination of charges at the interface between ZnO nanorods and I^-/I_3^- electrolyte. Interface recombination loss is due to the uncovered oxide surface (with no dye molecule anchored on), where oxide contacts with electrolyte closely and thus increases the probability of charge recombination between electrons in oxide and holes in electrolyte. When light is absorbed the electrons are injected from the dye into the ZnO nanorods while the separated holes are transported to the counter electrode by means of redox process. The efficiency of charge collection is governed by the difference between the rate of charge transport and the rate of charge recombination. In order to compete with the relatively slow charge transport through the nanorod network, an exceedingly slow redox shuttle must be employed to hinder recombination. The presence of surface defects on the ZnO nanorods can also help charge recombination. The surface defect can act as traps where electrons can recombine with I_3^- in the electrolyte. Redox mediators with lower redox potential could be used to achieve larger open circuit voltage. To improve the efficiency the volatile liquid electrolyte can be replaced by nonvolatile or solid state electrolyte and an attempt can be made to improve the light absorption and quantum yield.

4 Conclusion

Dye-sensitized solar cells have been fabricated using ZnO nanorod arrays vertically grown on indium tin oxide (ITO) glass substrate using a chemical method and natural dyes

extracted from Ixora coccinea, Mulberry and Beetroot dye as sensitizers. The dyes strongly absorb visible light having wavelength lying in region 400 and 550 nm. The solar cell efficiency has been calculated and is found to be $\eta = 0.33\%$, $\eta = 0.41\%$ and $\eta = 0.28\%$ for Ixora coccinea, Mulberry and Beetroot dye based solar cells. Preliminary test on the stability of the used natural dyes were carried out by monitoring some of the indicative parameters like open circuit voltage, short circuit current and efficiency under AM 1.5 solar irradiation for 6 h and no significant changes were observed.

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