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Highly efficient, optically semi-transparent, ZnO-based dye-sensitized solar cells with Indoline D-358 as the dye

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ABSTRACT

Highly compact, transparent, ZnO films have been prepared, on fluorine-doped tin(IV) oxide (FTO) glass plates, from 30 nm colloidal ZnO solution, with the help of novel atomized-spray pyrolysis (ASP) deposition technique. These films were used to construct dye-sensitized solar cells (DSCs) with Indoline D-358 as the dye. The DSC shows an optical transmittance of approximately 40% in the visible range. The cells show impressive solar cell parameters of 635 mV open circuit photovoltage (V_{oc}), 15.0 mA cm^{-2} of short-circuit current density (J_{sc}) and 0.62 fill factor (FF), with an overall efficiency (η) of 5.9% under air mass (AM) 1.5 illumination.

1. Introduction

Dye-sensitized photovoltaic cells fabricated utilizing pigments for trapping sunlight continue to receive attention as promising systems for the conversion of solar energy into electricity. This is due to their simplicity, low cost and reasonably good power conversion efficiency. Such artificial solar energy conversion devices were a mere curiosity until late nineteen eighties, because of their low energy conversion and low quantum efficiencies [1–6]. A major breakthrough that changed the situation was the observation that nanocrystalline and porous semiconductor films of large surface area could produce higher solar-to-electricity conversion efficiencies [7–9]. A typical DSC is comprised of a dye-absorbed porous nanocrystalline semiconductor film deposited on a conducting glass plate, a lightly platinized counter electrode, and an electrolyte containing I^-/I_3^- redox couple sandwiched between the electrodes. The dye sensitizer absorbs photons and the resulting excited state injects electrons to the conduction band of the semiconductor. The resultant oxidized dye is quickly reduced back to its original state by the reduced species in the electrolyte. The oxidized species of the redox couple is reduced back at the counter electrode. A crucial factor affecting the overall efficiency of the solar cell is the morphology of the semiconductor film. A high surface area is required to obtain a high light absorption from a single monolayer of the sensitizer dye which is adsorbed on the semiconductor surface. In order for the electrons injected to the conduction band of the semiconductor to move fast towards the back contact, the nature of the semiconductor film is crucial. Highly compact interconnected small nanoparticles in the film contribute not only to high electron conductivity but also to the increased surface area for dye absorption. The smaller particles (<100 nm) in the film allow for the light to pass through them, without significant scattering, resulting in a semi-transparent thin film. DSCs based on nanostructured TiO_2 are the most investigated systems to-date and are the most efficient ones. For example, the DSCs made with TiO_2 and porphyrin dyes have resulted in efficiency up to 11% [10–12]. However, from a fundamental point of view, ZnO with its band gap energy of 3.2 eV, and having band positions similar to those of TiO_2 but with higher electron mobility, 115–155 cm^2 V^{-1} s^{-1} compared to 10^{-5} cm^2 V^{-1} s^{-1} of TiO_2, should give equal or better solar cell performance.

There have been a considerable number of attempts made to use ZnO in DSCs. The preparation techniques used span a wide range of thin film deposition methods which involve electrodeposition [13], sol–gel techniques [14] and screen printing [15]. The maximum efficiency reported so far is for the cell fabricated using sol–gel deposited ZnO and ruthenium dye, which is around 5% [16]. Electrodeposition of ZnO in the presence of various dyes has been explored by Yoshida et al. who have reported 5.56% efficiency for the ZnO-Indoline D-149 dye combination [17]. Out of these techniques, screen printing and spray technologies give crack-free and compact thin films. However, particle aggregation reduces the surface area due to the formation of larger particles and hence the films become translucent or opaque. To rectify these problems, we have designed and developed a novel spray pyrolysis technique called

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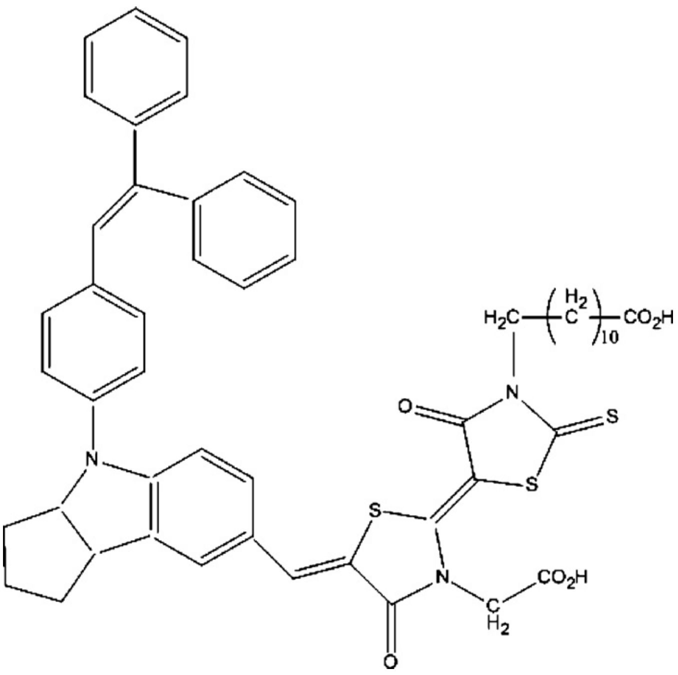

Fig. 1. Molecular structure of Indoline D-358 dye.

the "atomized spray pyrolysis (ASP)" where the colloidal solution aspirated impinges on a spherule which breaks any aggregates and individual particles get deposited in the thin film.

Conventionally used ruthenium complex dyes are not suitable for cost-effective, environmentally friendly photovoltaic systems, because of the rareness and high cost of ruthenium metal. Recently, a metal-free Indoline dye (D-358) (Fig. 1) having a high-extinction coefficient of 67000 M^{-1} cm^{-1} at 532 nm (as reported by the company) has been prepared by the Mitshubishi Paper Mills Limited. In this paper, we present the preparation of crack-free, semi-transparent thin films of ZnO without particle aggregation and their DSC applications with the metal-free Indoline D-358 dye.

2. Experimental

2.1. Preparation of semi-transparent ZnO film

All chemicals used were purchased from Wako Chemicals, Japan, unless otherwise stated. ZnO powder (30 nm, 0.6 g), glacial acetic acid (10 drops) and ethanol (40 ml) were mixed and ultrasonically dispersed for 10 min. Then the solution mixture was sprayed onto heated (150 °C) FTO glass substrate using the ASP machine and subsequently sintered in air at 500 °C for 30 min.

2.2. Dye adsorption

The semi-transparent ZnO electrode, pre-heated to 80 °C, was immersed in a mixture of acetonitrile/tert-butyl alcohol (volume 1:1) containing 3×10^{-4} M Indoline D-358 for 12 h. The plates were removed and rinsed with acetonirtrile and allowed to dry in air. The amount of adsorbed dye was determined by spectroscopic measurement of dye desorbed from the film surface. This was done by treating with NaOH (0.1 M) in a mixture of water and ethanol (50:50 by volume) and determining spectroscopically the amount of dye present in the solution. The calibration plot used was constructed by measuring light absorption at 532 nm of the standard dye samples. The straight line behavior of absorbance vs concentration of the dye gave validation to the applicability of the Beer–Lambert law. From the dye concentration in the test solution the amount of dye adsorbed on our ZnO film is 9.87×10^{-8} mol cm^{-2}.

2.3. Preparation of transparent Pt counter electrode

A solution of hexachloroplatinic acid in isopropanol (5 mM H_2PtCl_6) was prepared and a small amount of the solution was sprayed on to a pre-heated FTO glass plate (150 °C) and sintered at 400 °C for 15 min to give lightly platinized transparent FTO counter electrode.

2.4. Construction of the DSC

The dye-coated ZnO electrode was sandwiched with a transparent Pt counter electrode and the intervening space was filled with an electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M dimethylpropylimidazolium iodide in methoxyacetonitrile). The current–voltage (*I–V*) characteristics of the cells at AM 1.5 (100 mW cm^{-2}) simulated sunlight irradiation were recorded with a calibrated solar-cell evaluation system (PECell-PEC L 12). The active area was isolated using a black metal mask in order to avoid light scattering.

The particle size and surface morphology of the ZnO films were studied using Scanning Electron Microscopy (SEM, JOEL 6320 F). The transmittance and absorbance of the cell were measured using a Shimatzu UV 1800 spectrophotometer.

3. Results and discussion

SEM micrograph shows the surface morphology of semi-transparent ZnO film prepared by novel atomized-spray pyrolysis deposition technique (Fig. 2). It is clearly seen that ~30 nm particles are deposited in a compact manner forming a highly porous film. Fig. 3 shows the UV–visible absorption spectra of Indoline D-358 dye in t-butyl alcohol–acetonitrile (50:50) solution and that of the dye-adsorbed ZnO film. The shape of the absorption spectrum of Indoline D-358 adsorbed on the ZnO surface is almost the same as that of Indoline D-358 dye but with remarkable broadening. This broadening is a good indication of anchoring of the dye on to ZnO which is essential for vectorial transfer of electrons from the excited dye molecules to the CB of ZnO particles in the cell. The absorption peak maximum occurs at the wavelength (λ_{max}) of 532 nm. The extinction coefficient of D-358 has been observed to be 67000 M^{-1} cm^{-1}. This is much higher compared to

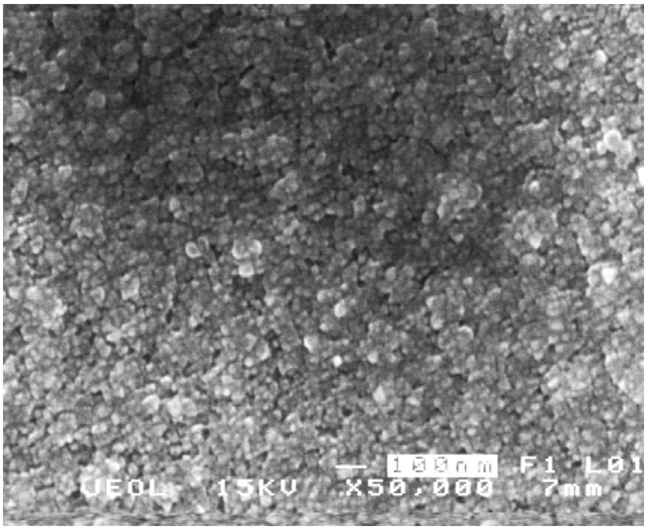

Fig. 2. SEM micrographs showing the surface morphology of semi-transparent ZnO film.

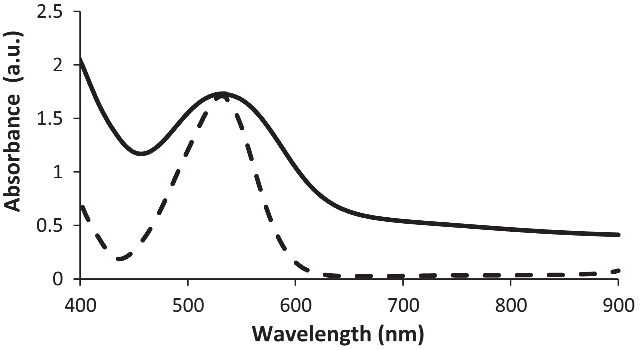

Fig. 3. Absorption spectra of Indoline D-358 dye in t-BuOH/CH_3CN (dashed line) and that of the dye-adsorbed ZnO film (solid line).

13900 $M^{-1}\,cm^{-1}$ at 541 nm for N719 dye under the same conditions [18]. Another remarkable property observed in the absorption spectra of the dye and dye-coated ZnO is that there are no peak shifts in the absorption maximum. Both materials give the same λ_{max} of 532 nm. This is a clear indication of the absence of H- and J-aggregates in the thin film of dye coated ZnO [19–21]. The absence of dye aggregates results in monolayer coverage of the dye on the ZnO particles which are anchored through the carboxylate group at a distance from the main chromopore seprated by 11 carbon methylene group spacer.

Fig. 4 shows the visible transmittance spectrum of a D-358 dye-sensitized ZnO solar cell. The average transmittance of over 30% is observed in the range of 650–900 nm. The dye absorbs light between 450 and 550 nm range and hence the transmittance in this range is reduced. It is interesting to note that the thickness of the ZnO layer measured using a digital micrometer gives around 12 μm which is comparable with usual thickness of around 15 μm used in conventional TiO_2 nanocrystalline electrodes. Though our cell produces over 30% transmittance above 550 nm, the usual ZnO cells are opaque. To our knowledge, this is the first time a semitransparent ZnO electrode was prepared and used in DSC applications. This is due to the ability of Atomized SPD technique we developed to deposit agglomeration free thin films with discrete particles which can be interconnected in the subsequent heat-treatment process.

The photovoltaic properties of the DSC were measured under AM 1.5 irradiation (100 $mW\,cm^{-2}$). Fig. 5 shows the *I–V* characteristics of a DSC having the highest performance. The cells show impressive parameters of 635 mV open circuit photovoltage (V_{oc}), 15.0 $mA\,cm^{-2}$ of short-circuit current density (J_{sc}) and 0.62 of fill factor (FF), with an overall efficiency (η) of 5.9% under air mass (AM) 1.5 illumination. In order to compare this performance with that of conventional ZnO films, a series of measurements were done using conventional ZnO films. DSCs made with conventional ZnO films show about 10 $mA\,cm^{-2}$ of J_{sc}, 0.506 V of V_{oc}, 0.56 of FF and efficiency of 2.6%. The impressive highest efficiency for ZnO DSC in our system is due to several reasons. The discrete, interconnected particles in the thin film give a large surface area for dye absorption. The dye absorption measured by the usual dye desorption procedure gives 9.87×10^{-8} $mol\,cm^{-2}$ which is slightly higher than the dye adsorption in the usual thin films of ZnO. The vectorial injection of electrons due to proper anchoring of the dye results an increased electron injection to give high photovoltage. The faster transport of the electrons along the interconnected discrete particles gives a high photocurrent density. Proper adhesion of the ZnO layer to the FTO surface provides a reasonably high fill factor. The increase in all these parameters collectively gives a cell with a high conversion efficiency of 5.9%.

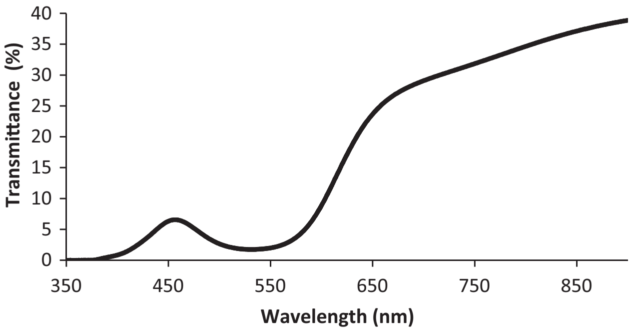

Fig. 4. Transmittance spectrum of a D-358 dye-sensitized ZnO solar cell.

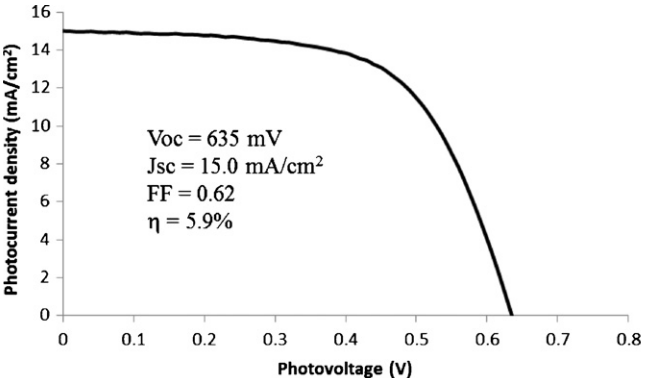

Fig. 5. *I–V* characteristics of the solar cell (cell area = 0.25 cm^{-2}) at AM 1.5 irradiation.

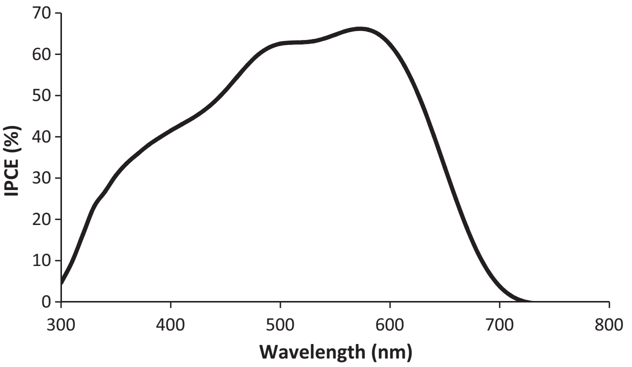

Fig. 6. Photo-current action spectrum showing the monochromatic incident photon to current conversion efficiency (IPCE) of the ZnO-based DSSC sensitized with D-358 dye.

The IPCE for our system is shown in Fig. 6. This spectrum clearly shows that the photons in the range 300–700 are converted to electrons. The IPCE goes above 60% in the wavelength range 480 nm to 610 nm.

4. Conclusion

In this work, we have prepared a highly efficient ZnO based solar cell with an Indoline dye D-358. The ZnO electrode is highly compact and consists of interconnected discrete particles without any particle agglomeration. UV–visible spectroscopy of the dye and dye-coated ZnO show the same absorption maximum indicating the absence of H- or J-aggregates. The latter is broader compared to the former which indicates that the dye is effectively anchored to the ZnO surface for efficient electron injection. The cell has over 30% transmission above 550 nm. This cell gives 5.9% overall conversion efficiency with J_{sc}, V_{oc} and FF of 15.0 $mA\,cm^{-2}$, 635 mV and 0.62 respectively.

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