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Al-doped ZnO thin films grown onto ITO substrates as photoanode in dye sensitized solar cell

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ABSTRACT

The photovoltaic performance of dye sensitized solar cells using Al-doped ZnO thin films (ZnO:Al) grown onto ITO substrates as photoanode and natural dye as sensitizer had been studied. The effects of [Al/Zn] ratio on structural, microstructural, optical and electrical properties of these films were investigated. X-ray diffraction analysis of pure and Al-doped ZnO thin films revealed the polycrystalline nature with wurtzite-type structure and preferential orientation along the c-axis. FESEM images revealed granular and porous nanostructure for lower content of Al, whereas nanosheet morphology for higher Al content. Uniform distribution of grains with columnar-like nanostructure was observed by AFM analysis and confirmed the c-axis orientation. EDAX analysis confirmed the presence of Zn and O along with dopant Al. Higher transmittance around 95% was observed for AZO film (1.5 at.%) in the visible region with an absorption edge around 350 nm, while band gap energy was found to vary in the range 3.26–3.42 eV. PL spectra exhibited a ultra-violet emission centered at 385 nm and an intense violet emission centered at 444 nm. A decrease in the electrical resistivity was noticed upto 1.5 at.% of Al doping and increased for further increase of Al content. Dye sensitized solar cell fabricated with pure and AZO films as photoanodes sensitized with different natural dye extracts showed improved cell performance.

1. Introduction

Dye sensitized solar cell (DSSC), a third generation of photovoltaic device developed by Gratzel et al., in the early 1991 had attracted considerable attention due to their low cost, environmental friendly compared to Si and other inorganic based semiconductor photovoltaic devices (O'Regan and Gratzel, 1991). Nanocrystalline porous natured oxide which is a semiconductor based on conducting glass plate as photoanode with the absorption of dye, electrolyte and counter electrode are the essential parts of DSSC. The dye used as a sensitizer in DSSC plays a major role in cell performance. Though, the maximum conversion efficiency of 11–12% is achieved with Ru complexes having an intense charge-transfer absorption and efficient metal-to-ligand charge transfer; the major disadvantages of Ru complexes are its cost, toxicity, rarity and systems complexity (Chiba et al., 2006; Buscaino et al., 2008; Nazeeruddin et al., 2005).

Researchers have focused their attention on natural dye as an alternative to artificial dye because of its easy availability, low cost, easy preparation, environmental friendly and biodegradable (Narayan, 2012). Several natural dye sensitizers have been used as sensitizer in DSSC such as anthocyanin (Alhamed et al., 2012), tannin (Kamel et al., 2005), chlorophyll (Hao et al., 2006), flavonoid (Keka et al., 2012), cyanine (Luo et al., 2009) and carotenoid (Rühle et al., 2010).

Various semiconducting metal oxides like TiO_2, SnO_2, In_2O_3 and Nb_2O_5 have been used as photoanode in DSSC. Among these metal oxides especially ZnO could be considered as potential and promising alternative photoanode for DSSCs because of its large bandgap energy (3.37 eV), high electron mobility, and electronic properties which are quite similar to that of TiO_2 (Lu et al., 2010). The fast electron transport due to its high electron mobility reduces the recombination loss and increases the photocurrent efficiency. ZnO films having large inner surface area can capture large amount of dye molecules adsorbed on the surface layer, which improves light harvesting efficiency and also reduces carrier recombination (Wu et al., 2007). Fang et al., have reported a new strategy for improving the power conversion efficiency of ZnO nanorod-based dye sensitized solar cells (Fang et al., 2014). An electrical conversion efficiency of 3.43% is achieved for a DSSC containing a 5 μm thick mesoporous F-ZnO photoanode prism arrays (Luo et al., 2011).

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Pure ZnO thin films are unstable due to changes in the surface conductance under oxygen chemisorption and adsorption. Various dopant elements like Al, Ga, In, Sn and Mn are used for n-type ZnO in order to improve its structural (phase formation, point defects such as vacancies), microstructural (shape, size, size distribution, agglomeration, chemical composition) optical and electrical properties (Kaid and Ashour, 2007). In particular Al, Ga and In doped ZnO films exhibit preferential orientation along c-axis (0 0 2) plane and are found to be useful for various practical application in solar cells, gas sensors, catalysts, photodetectors, electroluminescence display, etc. (Zhang and Que, 2010). Aluminum doped zinc oxide (AZO) thin films are attractive owing to their good optical and electrical properties, low resistivity, high conductance and high transparency, which is suitable for device applications.

Numerous techniques have been employed to produce Al-doped ZnO thin films such as chemical vapor deposition (CVD), pulsed laser deposition (PLD), atomic layer deposition (ALD), radio frequency magnetron sputtering, sol-gel, electrochemical bath deposition and spray pyrolysis. Among these methods, the spray technique is most widely used for the preparation of transparent conducting oxides (TCOs) because of its simplicity, inexpensive and possibility of large area coatings (Dghoughi et al., 2010).

In this present research work, highly transparent AZO thin films were deposited onto In-doped SnO_2 (ITO) substrates by spray pyrolysis at different doping concentration (0–2.5 at.%) and characterized. The physical properties and performance of the DSSCs fabricated using pure and Al doped ZnO thin films as photoanode and natural dye extracts as sensitizer were investigated.

2. Experimental part

2.1. Preparation of photoanodes

Pure and Al-doped ZnO thin films were deposited onto ITO glass substrates by spray pyrolysis. The starting solution was prepared by 0.1 M of $ZnC_{10}H_{14}O_5$ dissolving in ethanol. Aluminum chloride ($AlCl_3$) was used as a dopant source material with varying [Al]/[Zn] ratio in the range 0–2.5 at.%. ITO glass substrates were pre-cleaned with ethanol and acetone in an ultrasonic bath for 10 min and the films were deposited with the optimized substrate temperature 350 °C. The atomization of the solution into a spray of fine droplets was carried out by a spray nozzle, with the help of compressed air as a carrier gas. The spray time and spray rate were maintained at 3 ml/min and 30 min, respectively. The substrate-to-nozzle distance was kept at 23 cm vertically. The grown films had good adhesion to the substrate surfaces. The detailed experimental procedure and the spray parameters are discussed elsewhere (Dhamodharan et al., 2015a, 2015b).

2.2. Dye extraction

Anthocyanin and chlorophyll were extracted from capsicum, grapes, beetroot, red hibiscus (*Hibiscus rosasinensis*) and green pomegranate leaves by separately putting 10 g of *Hibiscus rosasinensis* and *pomegranate* in 10 ml of ethanol by indirect hydronic heating in boiling water for 30 min. Pure and natural dye solutions were obtained by filtering out the solid dregs (Fig. 1).

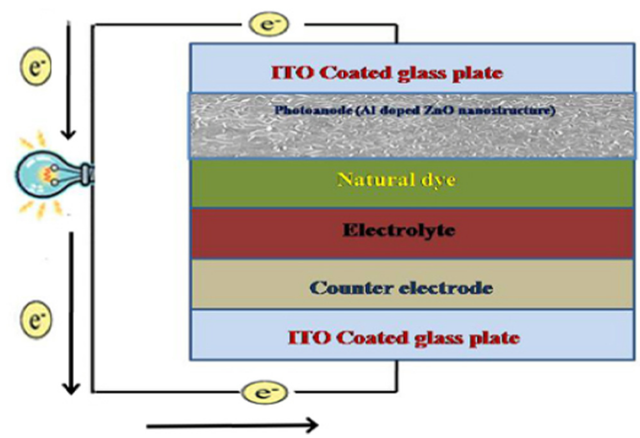

Fig. 2. Schematic diagram of dye sensitized solar cell.

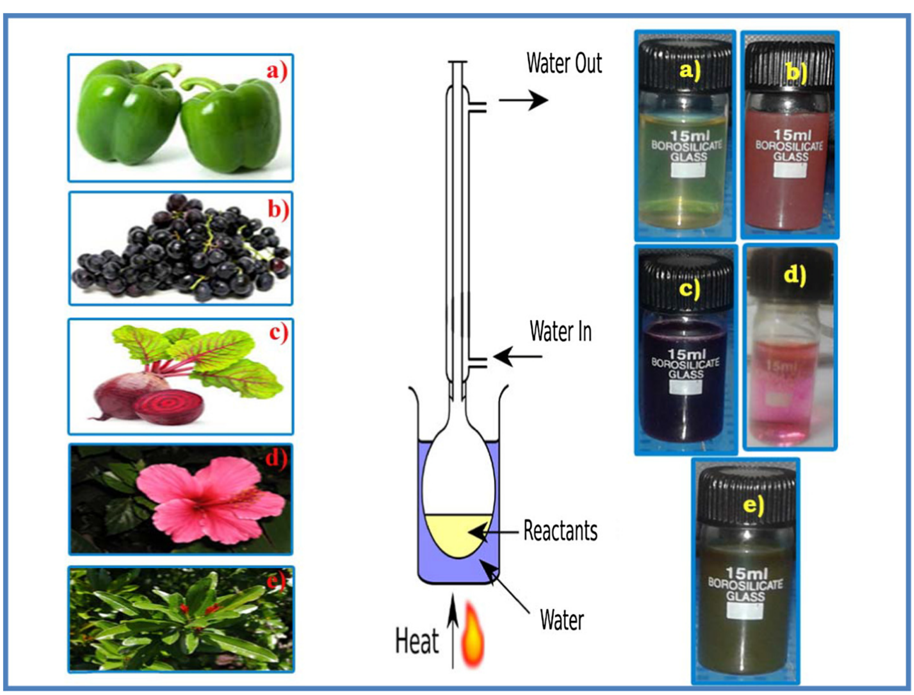

Fig. 1. Dye extract procedure (a) capsicum, (b) grabs, (c) beetroot, (d) hibiscus rosasinensis, (e) pomegranate.