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Natural dyes as photo-sensitizer in solar cells

Surendra Bikram Silwal[1,2,3], Rameshwar Adhikari[2], Prakash Lamichhane[3], Netra Lal Bhandari[1, 2*]

[1]Department of Chemistry, Tri-Chandra Multiple Campus, Tribhuvan University, Kathmandu, Nepal

[2]Research Centre for Applied Science and Technology (RECAST), Tribhuvan University, Kirtipur Kathmandu, Nepal

[3]Department of Chemical Science and Engineering, School of Engineering, Kathmandu University, Dhulikhel Kavre, Nepal

*Email: netra.tu.edu@gmail.com

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ABSTRACT

The objective of this research is to employ the natural dyes in dye-sensitized solar cell (DSSC). On account of eco-friendly, renewable, and non-hazardous properties of natural dyes over silicon, a semiconductor, photo-sensitizer in conventional solar cells, cyclohexane extract of *Terminalia alata*, a natural dye, was employed as photo-sensitizer. The photoanodes ZnO and 5% Al-doped ZnO for DSSCs were developed by spray pyrolysis. The X-ray diffraction (XRD) has shown hexagonal wurtzite structure of ZnO with lattice constants a = 3.2487 Å and b = 5.1518 Å having particle size 25.85 nm for ZnO and 33.17 nm for Al-doped ZnO. The DSSC properties such as solar conversion efficiency (η), short-circuit current density (Jsc), open-circuit voltage (Voc), and fill factor (FF) were found to be 0.31%, 2.10 mA/cm^2, 0.73V, and 45% for ZnO photoanode and 0.37%, 2.25mA/cm^2, 0.70 V, and 52.10% for 5% Al-doped photoanode respectively.

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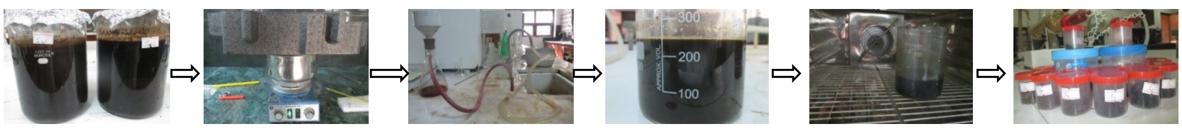
1. Introduction

The global energy demand is rocketing, it was 12.7 TW (terawatt, 1 TW = 1012 W) in 1998 but is expected to be 26.4 to 32.9 TW in 2050 and 46.3 to 58.7 TW in 2100 [1]. Since the fossil fuels are non-renewable and will suffice for merely few decades, solar energy, best option so far, is one of the major viable, eco-friendly, and renewable, alternative source of energy. As it is said, "*More energy from sunlight strikes Earth in 1 hour than all of the energy consumed by humans in an entire year.*" [2], solar energy can sustainably be harvested for human civilization. A solar cell is an electrical device that converts sunlight directly into electricity by photovoltaic effect whose production has been exponentially increasing [3].

A dye-sensitized solar cell (DSSC), first developed by Gratzel et al. in 1991 [4], is an electrical device which converts light photons into electricity by photovoltaic effect, incorporating oxide semiconductor like TiO_2, ZnO, Nb_2O_5, etc. with wide band gap ≥3 eV as photoelectrode and dye molecules as photo-sensitizer. Since natural dyes are more economical, easily attainable, abundant in supply, non-hazardous, eco-friendly, and renewable, fabricating an environment friendly DSSC, more precisely natural dye-sensitized solar cell (NDSSC), are both technically and economically credible alternative to p-n junction silicon solar cells [1]. The objective of this research is to strive n-type doping of ZnO, a semiconductor, with aluminum and observe its optical, structural properties; and their effect on DSSC properties employing natural dye as photo-sensitizer.

2. Materials and Method

A natural red dye from the bark of *Terminalia alata* (local name: Saaj), a photo-sensitizer for DSSC, was extracted on both polar solvent, water as shown in Figure 1, and non-polar solvent, cyclohexane, to compare their UV-visible absorption spectra obtained by using UV-1800 spectrophotometer of SHIMADZU CORP. (05103).



Soaking 80 g of crude dye sample in 800 ml water in 1000 mL ⇨ Heating the soaked sample in electric heater at 80^0C for 2 hours ⇨ Filtering the dye sample through Whatman No.1 filter paper under suction ⇨ Filtrate of aqueous dye extract ⇨ Keeping the concentrated dye extract in hot air oven to get powder dye ⇨ Dried aqueous extracts of all six dye samples

Fig. 1: Flow chart showing different steps in aqueous extraction of natural dye.

For dye-sensitized solar cell (DSSC), ZnO and 5% Al-doped ZnO photoanodes were fabricated by spray pyrolysis of precursors on fluorine doped tin oxide (FTO) glass sheets with 8 Ω/sq. surface resistivity. The spray pyrolysis is a technique in which chemical precursors are atomized into aerosol droplets and sprayed over a highly heated substrate so that the solution of undesired compounds get evaporated leaving behind the ultrafine particles of required compound which on sintering at above 400^{o}C forms a thin film. The precursor for ZnO fabrication, 100 mL 0.3 M $Zn(CH_3CO_2)_2$ (zinc acetate) solution, was prepared by dissolving 6.7125 g of Merck 98% zinc acetate in 100 ml solvent of propan-2-ol and distilled water in the ratio 3:1. To make a clear solution, the solution was continuously stirred keeping over magnetic stirrer with hot plate for 30 minutes and remaining little white turbidity of zinc acetate was dissociated by adding few drops of acetic acid. And for 5% Al-doped ZnO, 0.2 g of $AlCl_3$ (aluminum chloride) was dissolved in 100 ml of 0.3 M zinc acetate solution.

During spray pyrolysis, the aerosol of zinc acetate was created by using an ultrasonic nebulizer which was sprayed vertically through a spray nozzle on the heated FTO substrate, 25 × 25 mm^2, placed on a heating block of temperature 400^{o}C. The FTO substrate was maintained to move in a 2×2 matrix pathway at a fixed frequency by an electronically controlled motor keeping the spray nozzle to FTO's height 6 cm and spraying rate 40 ml/hr. The FTO substrate was sprayed over with precursor for 10 minutes and sintered at 500^{o}C for 30 minutes in muffle furnace. After 30 minutes of sintering, the substrate was sprayed over again for 5 minutes and then sintered for 2 hours facilitating the deposition of ZnO particles on FTO. And for the 5% Al-doped ZnO fabrication, the FTO substrate was sprayed over with zinc acetate solution for 10 minutes, sintered at 500^{o}C for 30 minutes, after again sprayed over with 5% Al-doped zinc acetate for 5 minutes, and then sintered for 2 hours.

The transmittance of those fabricated thin films was measured by using Optical Profilometer (Spectroscopic reflectometer, SRM 300, Angstrom Sun Technology) and that of crystallographic structures by X-ray Diffraction (XRD) using Broker D2 Phaser (Cu Kαl, λ = 1.54060 Å).

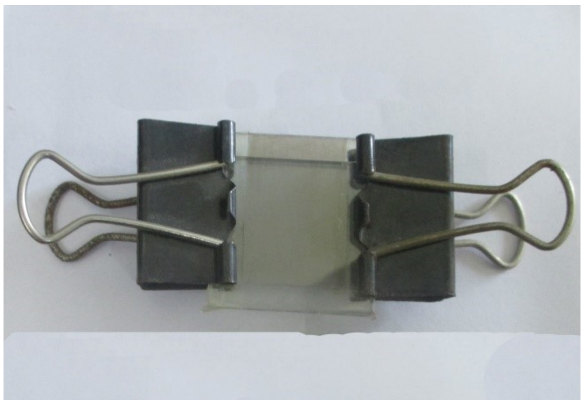


Fig.2: A typical dye-sensitized solar cell.

The redox electrolyte I^-/I_3^- couple was made by mixing 25 ml 0.05 M I_2 (Aldrich iodine) and 25 ml of 0.1M KI (potassium iodide) in acetonitrile with 20 mL of PEG (polyethylene glycol) as a binder. The counter electrode, cathode, was made by rubbing pencil graphite in the middle 25 × 25 mm^2 conducting side of the FTO glass sheet. The ZnO and 5% Al-doped ZnO fabricated FTO substrates, photoanodes, were dipped in cyclohexane extract of natural red dye from the bark of *Terminalia alata* for 12 hours, then taken out, dried, and reduced to 15 × 15 mm^2 leaving each side 0.5 mm using forceps with conc. HCl. The opposite two sides of each FTO substrate were masked with plastic tape, few drops of redox electrolyte was poured and allowed to spread all over. Then the counter electrode, cathode, was gently placed over the photoanode and tightly sealed using alligator clips as shown in Figure 2. The photovoltaic parameters of such fabricated DSSC were measured by using Kiethley Source Meter (A Tektronix Company) maintaining 1000 W/m^2 incident light intensity.

3. Results and Discussion

The UV-visible spectra of cyclohexane extract, CS, from the bark of *Terminalia alata*, were found to be comparatively better than of aqueous extract, S, as shown in Figure 3(a) so CS was used as photo-sensitizer in DSSC. The absorbance peaks of employed sensitizer dye sample, S, has shown peaks in 675 nm and 415nm which are similar to the peaks of both ZnO and 5% Al-doped ZnO thin films as shown in Figure 3(b).

The optical transmittance of FTO was above 80% and it has reduced to 50% after coating ZnO for 15 minutes, but for the same duration of coating, the transmittance of 5% Al-doped ZnO thin film is found to be 55% as shown in Figure 4(a). The 5% more transparency of Al-doped ZnO may be due to the formation of more porous thin film by Al-doping.

The XRD peaks, as shown in Figure 4(b), have been identified to (100), (002), (101), (102), (103) and (112) plane of reflections which are in agreement with the joint committee on powder diffraction standards (JCPDS) data for a single phase wurtzite structure of ZnO. The XRD of undoped ZnO has shown preferential orientation of grains along the c-axis, perpendicular to the film surface (002), whereas, the aluminum doping has resulted random orientation of peaks. The rest unmarked major peaks oriented to (200), (211) etc. seen in the XRD spectra are contributed by the FTO.

The mean crystalline size of the ZnO particles is calculated by using Scherrer formula [5], $D = \frac{0.9\lambda}{\beta\cos\theta}$, and found to be 25.85 nm for undoped ZnO and 33.17 nm for Al-doped ZnO. Similarly, the lattice constants of deposited ZnO particles are calculated, found to be a = 3.2487 Å and b = 5.1518 Å which are in agreement with JCPDS data values for ZnO lattice constants, a = 3.24982 Å and c = 5.20661 Å.

Current-voltage Curve Analysis

A current-voltage (IV) curve is obtained by plotting short-circuit current density (Jsc) against open-circuit voltage (Voc) [6] as shown in Figure 5.

The values of Voc, Vmax, Jsc and Jmax are obtained from IV curve. The fill factor (FF) and solar conversion efficiency (η) have calculated using the formulae $FF = \frac{Jmax \times Vmax}{Jsc \times Voc}$, and, $\eta = \frac{Jsc \times Voc \times FF}{Is}$, and obtained values are tabulated in Table 2.

The efficiency of Saaj-sensitized solar cell based on Al-doped ZnO photoanode, 0.37%, is found to be slightly greater than that of ZnO photoanode, 0.31%, possibly due to increase in the particle size of ZnO from 25.85 nm to 33.17 nm with Al-doping. The increased particle size enhances the porosity and transparency of thin film which facilitates the more light intensity to the dye molecules (sensitizers) to generate more electrons. Thus by generating more electrons, Al-doping has increased the cell's efficiency. However, the overall poor efficiency of natural dye-sensitized solar cell may be attributed to the poor transmittance, ≤ 55%, and improper thickness of the fabricated oxide film, insufficient adsorption of dye molecules, poor absorbance of dye molecules in visible region, or may be because of poor performance of redox electrolyte and counter electrode. Those limitations, nevertheless, can be overcome by tailoring optoelectronic properties of dyes and modifying the cell's components, for example, incorporation of nanoparticles or quantum dots into photoelectrodes, molecular engineering of the natural dye molecules, etc.

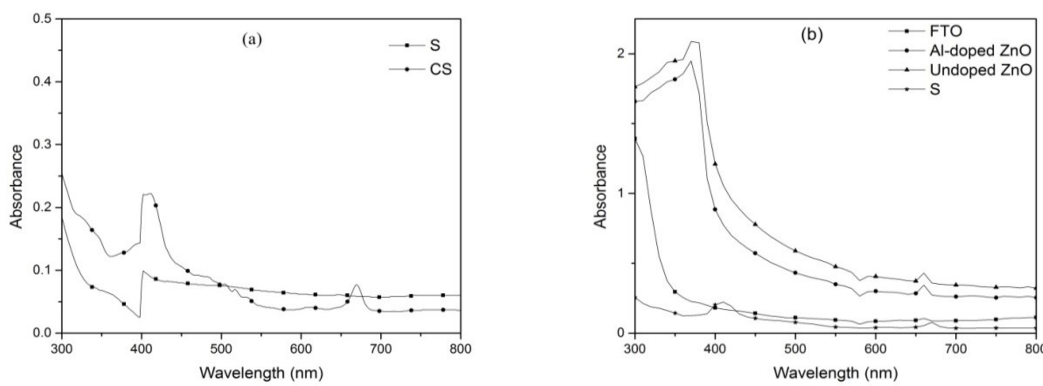


Fig. 3: UV-visible spectra of (a) aqueous extract (S) and cyclohexane extract (CS) of natural dye sample and (b) FTO, ZnO, 5% Al-doped ZnO thin film and natural dye sample.

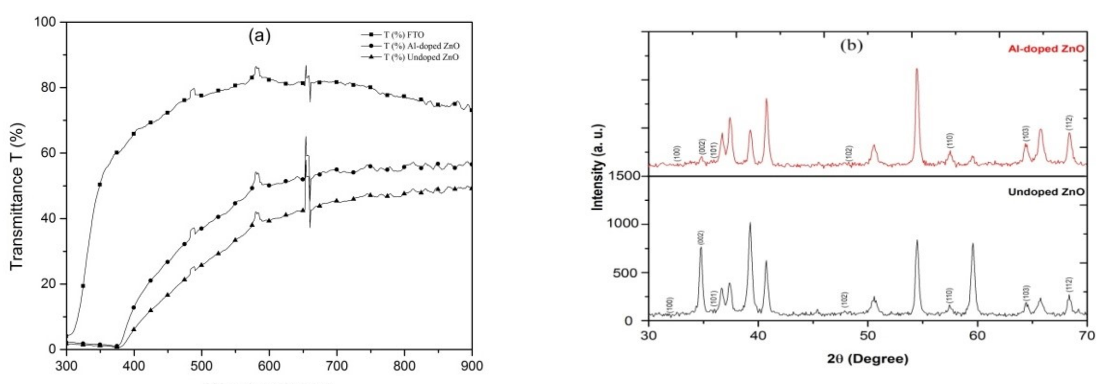
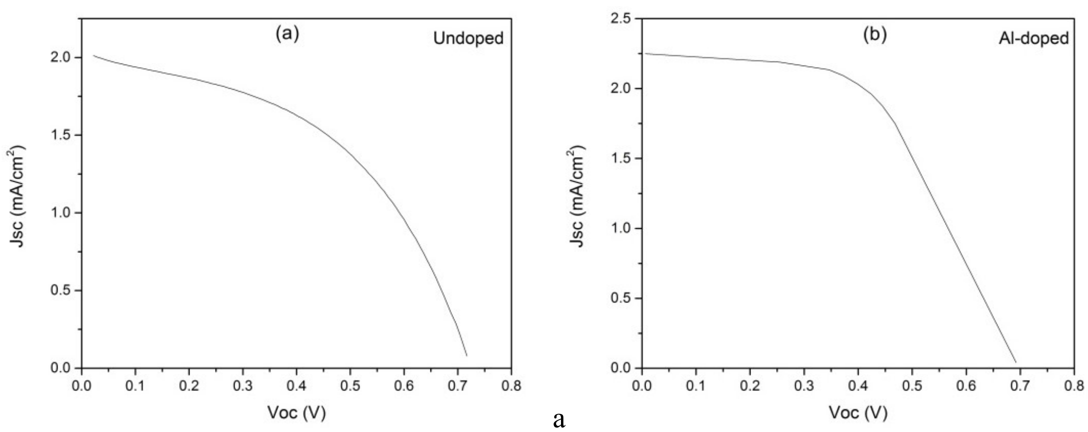


Fig. 4: Plots of (a) Transmittance of FTO, ZnO and 5% Al-doped ZnO thin film and (b) XRD pattern of Al-doped and undoped ZnO nanoparticles along with fluorine doped tin oxide (FTO).

Table 1: Interplanar spacing (d_{hkl}) from XRD spectra of ZnO particles.

2θ (degree)	Miller indices (hkl)	Calculated d_{hkl} (Å)	JCPDS d_{hkl} (Å)
31.78	100	2.8135	2.81179
34.80	002	2.5759	2.6049
36.33	101	2.4709	2.4786
47.54	102	1.9111	1.9128
57.52	110	1.6005	1.6269
64.21	103	1.4494	1.4784
68.02	112	1.3772	1.3799



a

Fig. 5: IV curve of Saaj-sensitized solar cell based on (a) undoped ZnO and (b) 5% Al-doped ZnO photoanode.

Table 2: Photovoltaic parameters of Saaj-sensitized solar cell

Sample	Jsc (mA/cm^2)	Voc (V)	Pmax	FF (%)	Efficiency (η)
Saaj (Undoped ZnO)	2.10	0.73	0.69	45.00	0.31
Saaj (Al-doped ZnO)	2.25	0.70	0.82	52.10	0.37

4. Conclusions

The cyclohexane extract of red dye from the bark of *Terminalia alata* gave relatively better absorbance than aqueous extract, so, employed as photo-sensitizer. The ZnO and 5% Al-doped ZnO thin films developed by spray pyrolysis technique have shown transmittance 50% and 55% respectively. The XRD of ZnO has shown hexagonal wurtzite structure with lattice constants a = 3.2487 Å and b = 5.1518 Å having particle size 25.85 nm for undoped ZnO and 33.17 nm for Al-doped ZnO. Thus, natural red dye-sensitized solar cell has given 0.31% solar conversion efficiency (η) incorporating ZnO photoanode with 2.10 mA/cm^2 short-circuit current density (Jsc), 0.73 V open-circuit voltage (Voc) and 45% fill factor (FF), and 0.37% efficiency incorporating 5% Al-doped ZnO photoanode with 2.25mA/cm^2 Jsc, 0.70 V Voc and 52.10% FF.

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References

[1] A. N. B. Zulkifili, T. Kento, M. Daiki, and A. Fujiki, The basic research on the dye-sensitized solar cells (DSSC), Journal of Clean Energy Technologies 3 (5) (2015) 382-386.

[2] K. E. Jasim, Dye Sensitized Solar Cells - Working principles, challenges and opportunities, IntechOpen (2011) 171-198. https://doi.org/10.5772/19749.

[3] W. Ghann, H. Kang, T. Sheikh, S. Yadav, T. C. Gil, F. Nesbitt, and J. Uddin, Fabrication, optimization and characterization of natural dye sensitized solar cell, Scientific Reports 7 (41470) (2017) 1-11. https://doi.org/doi10.1038/srep41470.

[4] M. Gratzel, Dye-sensitized solar cells, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 4 (2003) 145–153.

[5] R. Ayouchi, d. Leinen, F. Martin, M. Gabas, E. Dalchiele, and J. R. R. Barrado, Preparation and characterization of transparent ZnO thin films obtained by spray pyrolysis, Thin Solid Films 426 (2003) 68-77.

[6] I. Jinchu, C. O. Sreekala, and K. S. Sreelatha, Dye sensitized solar cell using natural dyes as chromophores – review, Materials Science Forum 771 (2014) 39-51.

[7] G. Calogero, G. D. Marco, S. Caramori, S. Cazzanti, R. Argazzic, and C. A. Bignozzi, Natural dye senstizers for photoelectrochemical cells, Energy and Environmental Science 2 (2009) 1162–1172. https://doi.org/10.1039/b913248c.

[8] T. Prasada and M. C. Santhoshkumar, Effect of thickness on structural, optical and electrical properties of nanostructured ZnO thin films by spray pyrolysis, Applied Surface Science 255 (2009) 4579-4584.

[9] P. Bindu and S. Thomas, Estimation of lattice strain in ZnO nanoparticles: X-ray peak profile analysis, Theoretical and Applied Physics 8 (2014) 123-134. https://doi.org/10.1007/s40094-014-0141-9.

[10] B. J. Lokhande, P. S. Patil, and M. D. Uplane, Studies on structural, optical and electrical properties of zinc oxide films prepared by spray pyrolysis technique, Physica B 302 (2001) 59- 63.

[11] S. Ilican, M. Caglar, and Y. Caglar, Determination of the thickness and optical constants of transparent indium-doped ZnO thin films by the envelope method, Materials Science-Poland 25 (3) (2007) 709-717.

[12] G. G. Valle, P. Hammer, S. H. Pulcinelli, and C. V. Santilli, Transparent and conductive ZnO:Al thin films prepared by sol-gel dip-coating, Journal of European Ceramic Society 24 (2004) 1009-1013.

[13] L. E. Mir, Z. B. Ayadi, M. Saadoun, K. Djessas, H. J. V. Bardeleben, and S. Alaya, Preparation and characterization of n-type conductive (Al, Co) co-doped ZnO thin films deposited by sputtering from aerogel nanopowders, Applied Surface Science 254 (2007) 570-573.

[14] H. Zhou, L. Wu, Y. Gao, and T. Ma, Dye-sensitized solar cells using 20 natural dyes as sensitizers, Journal of Photochemistry and Photobiology A, 219 (2011) 188-194,.

[15] X. F. Wang and O. Kitao, Natural chlorophyll-related porphyrins and chlorins for dye-sensitized solar cells, Molecules 17 (2012) 4484-4497. https://doi.org/10.3390/molecules17044484.

[16] C. S. Prajapati, A. Kushwaha, and P. P. Sahay, Experimental investigation of spray-deposited Fe-doped ZnO nanoparticle thin films: structural, microstructural, and optical properties, Journal of Thermal Spray Technology (2013). https://doi.org/10.1007/s11666-013-9973-0.

[17] Y. E. Morales, J. Reyes, B. Hermosin, and J. A. A. Barrios, Characterization of a natural dye by spectroscopic and chromatographic techniques, Materials Research Society, 1374 (2012) 1-10. https://doi.org/10.1557/opl.2012.1377.