

Enhancing the performance of TiO₂ based N-DSSC using dye extracted from *Tabernaemontana divaricata*, *Dypsis lutescens* and mixed sensitizer.

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Abstract- Two different natural dyes, such as *Tabernaemontana divaricata* (white flower), *Dypsis lutescens* (Green, leaf), were extracted to fabricate natural dye-sensitized solar cell (N-DSSC) with standard TiO₂ nanoparticles (p25) on the FTO substrate using doctorblade method as a photoanode. Optical and electrical properties were carried out for comparative study of fabricated photoanode. Significant absorption in the visible region has been attained in photo-anodes, which was confirmed with an optical band gap reported from UV reflectance spectra. FT-IR studies were performed for the extracted dye for the chemical elucidation of presence of favourable functional groups that ensures the anchoring capability of dye molecule towards the TiO₂ particle.

INTRODUCTION:

The global energy consumption is increasing year by year. In 1998, it was 12.7TW, but in 2050, it is expected to be around 26.4 to 32.9TW and in 2100, it will increase up to 46.3 to 58.7TW [1]. The yearly increase in global energy consumption will result in the rise of demands towards natural resources such as coal, petroleum and natural gas. These natural resources will take thousand of years to form and it cannot be replaced as fast as they are being consumed. Therefore, it is possible that problems may arrive where we will be facing the shortage of resources which at the same time will caused in the rise of the harvesting expenses. As a result, the reliability on the other sources of energy, which is renewable will also rise [2].

The dye-sensitized solar cells (DSSC) which belong to the thin film group, emerged as a new class of low cost energy conversion devices with simple manufacturing procedures. Incorporation of dye molecules in some wide bandgap semiconductor electrodes was a key factor in developing photoelectrochemical solar cells. Since the low cost solar cells have been the subject of intensive research work for the last three decades [3]. DSSC consist of four components namely photoanode, dye, electrolyte and counter electrode. Photoanode is a transparent conductive oxide on glass substrate by coating a layer of n-type semiconductor material, typical semiconductor metal oxide by doctor blade method, printing method, spin coating etc. A layer of dye on the surface of semiconductor to absorb the photons from sunlight, namely synthetic dye [rutheniumbased dye] or natural dyes namely chlorophyll, anthocyanin and this forms the photoanode of the device [4][5].

Recently, titanium dioxide (TiO₂) has attracted attention from researchers worldwide due to its potential applications in environmental protection and energy generation and has been applied largely in DSSC due to its nanocrystalline mesoporous nature that translates to high surface area for dye adsorption. The absorbed dye molecules can then be excited by the solar energy to generate electron-hole pairs that are subsequently separated and transported within the lattice of TiO₂[6]. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO₂ are important parameters in determining the efficiency of the cell [7]. Since the dye plays an important role in absorbing visible light and transferring photon energy into electricity, much attention has been paid to survey the effective sensitizer dyes [8].

A large variety of photosensitizers, including synthetic as well as natural dyes, have been investigated for DSSCs. Synthetic dyes can, again, be classified into organometallic and organic dyes. Organometallic dyes contain transition metals within their structures, whereas organic dyes contain various organic chromophores. The most propitious sensitizers, in terms of efficiency and stability, are the Ru-bipyridyl compounds. These dyes have many advantages, such as stability, absorption of light in the visible range of the solar spectrum, and smooth electron injection and transportation. Even though Ru-based dyes can yield high PCEs, their preparations are multistep and time-consuming. Ru is also a rare metal and thus expensive. Scientists are looking for low-cost but efficient dyes as alternatives to Ru-based organometallic dyes [9].

In this work N-DSSC fabricated using dye extracted from ***Tabernaemontana divaricata* and *Dypsis lutescens*** using ethanol as a solvent. Mixed dye was prepared using two individual dye extract in ratio of 1:1. Bare photoanode is coated with TiO₂ using doctor blade method.

EXPERIMENT:**Preparation of natural dye:**

In this work using dye extract of *Tabernaemontana divaricata*, and *Dyopsis lutescens* were used. The flowers of *Tabernaemontana divaricata*(F) and the leaves of *Dyopsis lutescens*(L), each weighing 50 g, were taken individually in order to extract these sensitizers. It was kept in the dark and soaked in 100 ml of ethanol for one day [10]. The obtained solution is then purified using Whatman filter paper. The final dye extract from *Tabernaemontana divaricata*, and *Dyopsis lutescens* is represented as F and L sensitizer. Fig 1(a) & 1(b)

Preparation of Photoanode:

Transparent conductive oxide (TCO), which serves as the electrodes' main layer, is a key component of the working electrode in the transport of electrons. Transparent conducting substrates (TCOs), which serve as the foundation for the construction of photo-anodes and counter electrodes, were made using fluorine-doped oxide (FTO) substrates. Acetone and ethanol were used to wash the FTO substrate individually over 20 minutes inside an ultrasonic bath [11]. By exposing the active layer to be coated with an area of 1cm² on the conducting side, the cleaned FTO substrate is then sealed with scotch tape to cover the residual film. The 0.1g of p25 was stirred while 20 ml of nitric acid and 10 ml of acetic acid were added, one drop at a time, to create the TiO₂ sol-gel paste. After three hours of stirring on a magnetic stirrer, a produced paste was deposited on an FTO substrate using the doctor blade procedure [12]. For 30 minutes, coated film was placed in a muffle furnace set at 450°C, then slowly cooled to ambient temperature. After the sensitising process, the bare p25 photo-anode is submerged for 24 hours in the filtrated dye solution and left in the dark to ensure successful dye loading [13]. Fig (2).

Preparation of Counter Electrode:

In a DSSC, the counter electrode's function is to retrieve an electron from the external circuit. Using six HB pencils and a candle flame, an FTO substrate with a carbon-coated conducting surface has been formed. This carbon-coated film underwent annealing at 450°C for 30 minutes before being progressively cooled to room temperature. To eliminate unreacted surface carbon, it was then gently dried after being rinsed with ethanol. Hence, carbon-coated counter electrode is utilised as CE to increase the cell's efficiency [14].

Preparation of Electrolyte:

The inner charge transmission from the photo-anode to the CE and dye regeneration are both significantly influenced by the electrolyte. Solvent, ionic conductor, and additives are the three main parts of liquid electrolytes, respectively. Acetonitrile-based liquid electrolytes were created by mixing 0.83 g (0.5 M) potassium iodide (KI) and 0.127 g (0.05 M) iodine without the use of additives [15]. The most plausible mechanism is that these additives attach to the TiO₂ surface and restrict active reduction sites or block I³⁻ from reaching the surface. Electrical parameters such as photocurrent density, which represents the charge transport between the redox couple, photo-voltage, which establishes the electrolyte's redox potential, and fill factor, which establishes the diffusion of charge carriers within the electrolyte, are all significantly influenced by the electrolyte.

Fabrication of N-DSSC:

The N-DSSC was assembled by placing the dye sensitized photoanode and CE in a sandwich manner, using binding clips and cascaded with liquid electrolyte. Such a way that dye sensitized photoanode will facing downwards on to the counter electrode. Assembled solar cell should be slightly offset to connect the crocodile clips as an output terminal evaluated using light.

Results and Discussion:**Characterization and measurement**

The UV and visible region absorption spectra for extracted dye and fabricated photoanode were studied using V-770 JASCO UV-VIS-NIR spectrophotometer. Quantitative analysis of presence of various chemical groups for the dye extract was studied using FP8300 JASCO FT-IR spectrometer. For the fabricated photoanode electronic structure (imperfection and impurities) were analysed by FP8300 spectrofluorometer. Current-voltage performance for the solar cell and efficiency was determined (ratio of the maximum output by the power of the incident light) using Keithley 6517-B electrometer as an input power source.

UV-Vis Spectroscopy:

UV-Vis spectroscopy is a technique that involves the measurement of the absorption or transmission of ultraviolet and visible light by a sample. The technique is widely used in chemistry, biochemistry, and materials science for qualitative and quantitative analysis of samples. Fig. (3), depicts the light absorption capability of extracted dyes *Tabernaemontana divaricata* (F), *Dyopsis lutescens* (L) and Mixed (M) as sensitizer, dye sensitized photoanode *Tabernaemontana divaricata* (FA), *Dyopsis lutescens* (LA), Mixed (MA) and bare TiO₂ photoanode (BA) are studied using UV-V is spectroscopy. It is readily apparent from the graph that the absorption of wavelength takes place from near ultra violet region and passes on to the visible region of the spectrum for all the extracted dyes. In general, the chlorophyll absorption ranges from 600 to 700nm in electromagnetic spectrum [16]. The sensitizer(L) makes the highest peak at 676nm and sensitizer(M) making the highest peaks at 367,718 and 670nm represents the presence of chlorophyll. The sensitizer (L) had made a wider and broader absorption levels in both UV and visible region of spectrum, this confirms that it has both active ingredients present in the individual dye and making it more efficient in light harvesting [17].

FT-IR spectroscopy:

FT-IR spectroscopy were studied for the elucidation of functional group of extracted dye and to analyses the electron transport rate. To enhance the electron transportation rate, the adsorption of the sensitizing dye to the TiO₂ surface should be high. For the effective adsorption, the dye molecules should possess some functional group, which leads to the photon to electron conversion rate [18]. It was mentioned in the previous report, presence of functional group such as hydroxyl (-OH), esters and carbonyl (C=O) in the dyes are responsible for chemical adsorption of dyes on the surface of nanostructured TiO₂ film [19,20,21].

FTIR spectra obtained are almost similar for all three sensitizers ranging from 4000 cm⁻¹ to 400 cm⁻¹. These shows the presence of functional groups. The four major peaks observed at F is at 3294.42cm⁻¹, 2970.38 cm⁻¹, 1041.56 cm⁻¹, 879.54 cm⁻¹. The similar peaks are absorbed for L at 3525.88 cm⁻¹, 2970.38 cm⁻¹, 1049.28 cm⁻¹, 878.54 cm⁻¹ and absorption for M at 3309.85cm⁻¹, 2970.38 cm⁻¹, 1041.56 cm⁻¹, 879.54 cm⁻¹. The appearance of the peaks at 3600cm⁻¹ to 3200 cm⁻¹ contributes to the strong bond appearance in the region. This peaks corresponds to the presence of intermolecular hydrogen bond O-H stretching vibration and the dye belongs to the phenol group. The appearance of the peaks at 3000cm⁻¹ to 2780 cm⁻¹ contributes to the medium bond appearance in the region. The peaks observed at 2970.38 cm⁻¹, corresponds to the presence of C-H stretching vibration and the dye belongs to the alkane group. The appearance of the peaks at 1040 cm⁻¹ to 1050cm⁻¹ contributes to the strong bond appearance in the region. The peaks observed at 1041.56 cm⁻¹, 1041.56 cm⁻¹ corresponds to the presence of C-O stretching vibration and the dye belongs to the primary alcohol group. The appearance of the peaks at 880cm⁻¹ to 870cm⁻¹ contributes to the strong bond appearance in the region. The peaks observed at 1049.28cm⁻¹, 1049.28cm⁻¹ corresponds to the presence of C=C bending vibration and the dye belongs to the alkene group. The extracted dye F, L, M confirms the presence of functional groups like O-H, C-H, C-O and C=C group. The presence of O-H group plays a major role in adsorption of dye onto the TiO₂ surface. Fig 4(a), 4(b) & 4(c).

Photoluminescence:

Photoluminescence emission spectra is widely used to investigate photo carrier generation, such as immigration, transfer and recombination. In this study it compares the separation efficiency of photogenerated electron and holes for the fabricated photoanode (FA, LA, MA). Fluorescence emission spectra was studied using 250nm at room temperature as an excitation source. In fig. (5), photoluminescence emission spectra showed similar kind of emission pattern for all the dye sensitized photoanode with varying intensity. The peak at 419nm could be attributed to the band-edge emission. Smaller peaks for all the three films are observed due to the transition involved in recombination of electron because of intrinsic oxygen vacancies and surface defects in the photoanode. Likewise, the peak at 475nm is due to back electron transport resulting in dark current in the device [22]. It is clear that intensity of emission spectra for FA has relatively lower intensity, which says that electrons and holes are very hard to recombine. Generally lower intensity value in PL refers to the less charge carrier recombination rate and more number of free electrons are available for the photoexcitation and therefore it increases the photocatalytic properties of the device. Hence, all the films, exhibit lower PL intensity value in the visible region of the spectrum and showed good photocatalytic properties. In addition, lower PL intensity indicates the longer lifetime of carrier thereby enhancing the Voc of the device. Therefore, all the fabricated dye sensitized photoanode can assist the free electron in effective light harvesting.

J-V characteristics:

The fig. (6) represents the J-V characteristics of TiO₂ based natural. The overall efficiency (η) for the cell was calculated from the following equation (1) and (2),

$$FF = \frac{I_{max} * V_{max}}{J_{sc} * V_{oc}} \quad \text{-----}(1)$$

$$\text{Power conversion efficiency } (\eta) = \frac{J_{sc} * V_{oc} * FF}{P_{in}} \quad \text{-----}(2)$$

here,

Maximum current density (J_{max}), maximum voltage (V_{max}), P_{in} is the radiation power incident on the cell, Short circuit current (J_{sc}), Open-circuit voltage (V_{oc}).

The electrical parameter for all the three fabricated N-DSSC (F, L, M) are calculated and listed in table 1. It is clearly seen that FA-DSSC exhibited maximum efficiency among the fabricated cell this is attributed to the large number of chlorophyll chelating with TiO₂ surface thereby creating a perfect pathway for the charge transfer and reducing the recombination effect. This is an evident that, the improved Voc and FF is due to reduce in recombination. Whereas, MA-DSSC shows lower conversion efficiency due to the absence or reduced bonding to the TiO₂ and low extinction coefficient value [23].

J_{sc} value is directly proportional to extinction coefficient value. In GA, large number of π conjugation links are available by the co sensitizer which results in higher coefficient extinction and thereby increase J_{sc} value. Hence higher efficiency of the solar cell is attributed to the effective transfer of electron and enhanced absorption in the visible region of the device. The J_{sc} and V_{oc} are the two significant parameters in determining the efficiency of the cell [24]. Photoconversion efficiency of fabricated N-DSSC are in the order of FA-DSSC (0.36%) < LA-DSSC (0.23%) < MA-DSSC (0.15%).

CONCLUSION:

N-DSSCs were successfully fabricated using extracted dyes *Tabernaemontana divaricata* (F), *Dypsis lutescens* (L), and mixed sensitizer (M). UV-Vis spectra revealed that, absorption rate of individual photoanode had a significant in harvesting the photons. FT-IR confirmed the presence of O-H group and C=O group in the extracted dyes, so that the dye molecules can bond with TiO₂ and transfer excited electron from sensitizer into the conduction band of metal oxide. Good photocatalytic properties have been exhibited by all three photoanode (such as LA, FA and MA) because of lower PL intensity. Significantly, J-V characteristics for FA incorporated N-DSSCs showing the efficiency (0.36%) than the other photoanode based N-DSSCs, i.e., PA and MA

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Fig. 1(a)

Fig. 1(b)



Fig. (2)

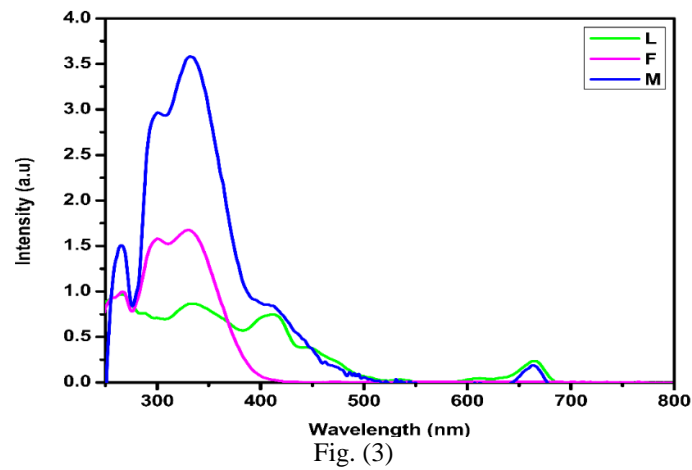


Fig. (3)

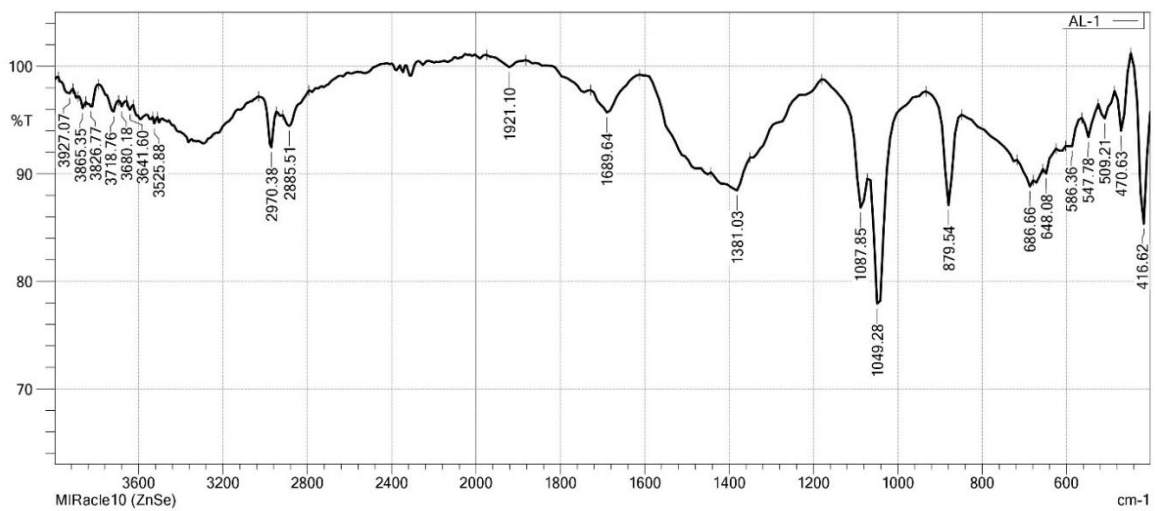


Fig. 4(a) (L)

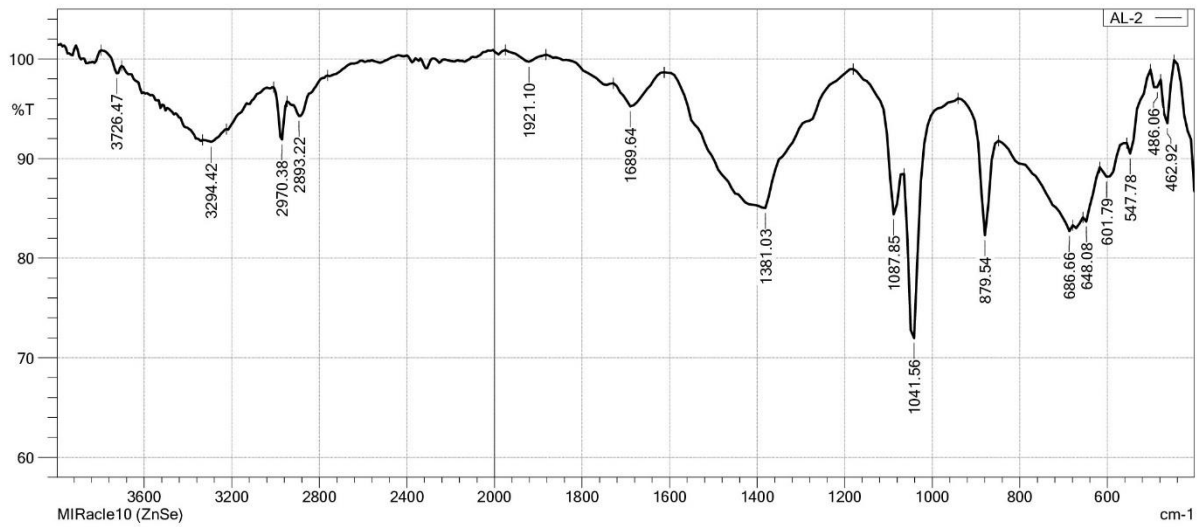


Fig. 4(b) (F)

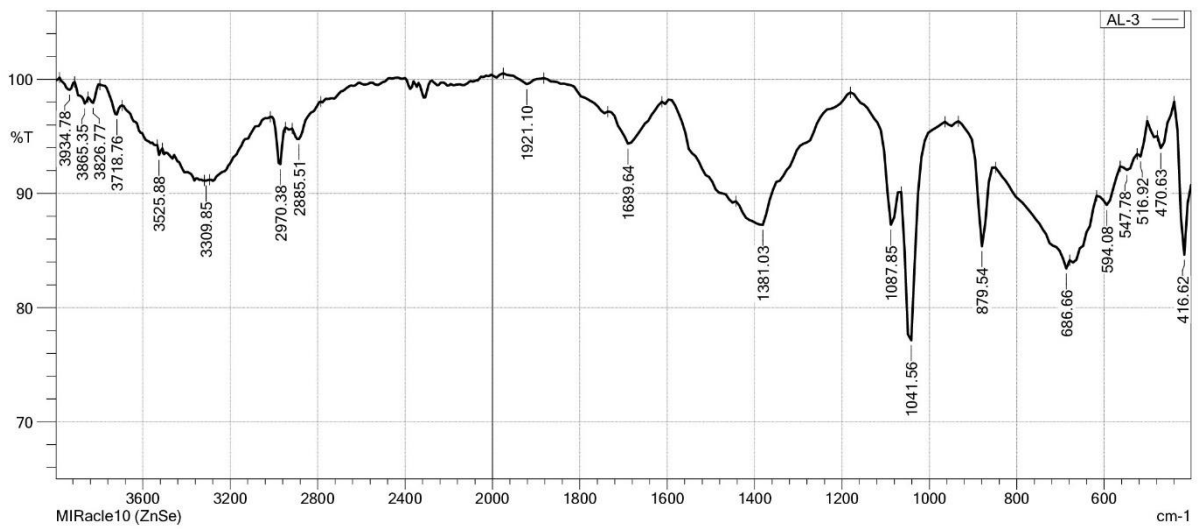


Fig. 4(c) (M)

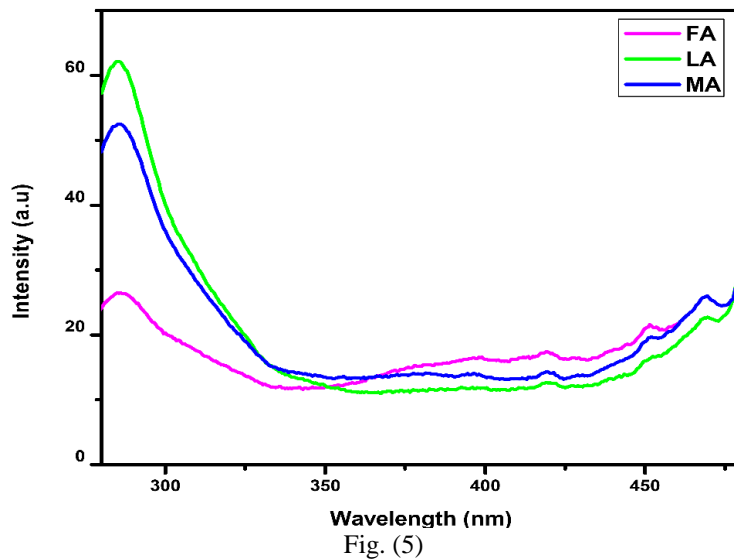


Fig. (5)

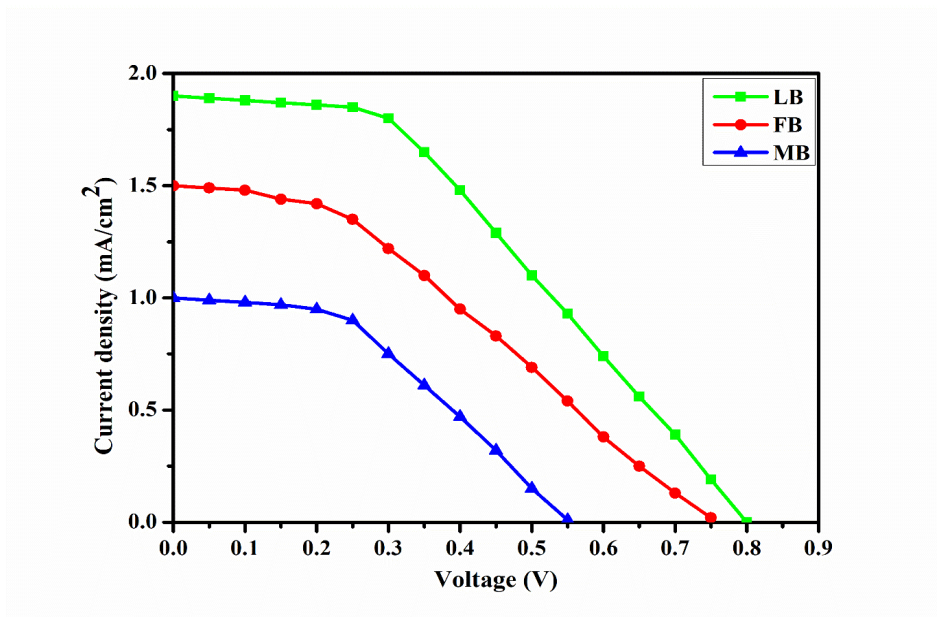


Fig. (6)

DSSCs based on Photo-anode		Jsc(mAcm ⁻²)	Voc (mV)	FF	η (%)
LEAF					
	LA	1.5	0.75	0.3	0.23
FLOWER					
	FA	1.9	0.3	0.355	0.36
MIXED					
	MA	1	0.55	0.409	0.15

Table.1