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Absorption Spectra of Natural Dyes and Their Effect on Efficiency of ZnO Based Dye-Sensitized Solar Cells

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Abstract

Natural dye-sensitized solar cells (DSSC) are one of the most promising devices for the solar energy conversion due to their low production cost and low environmental impact. The synthesis and performance study of Zinc oxide (ZnO) nanorods based DSSC is reported in the present paper. ZnO nanorods were fabricated using sol-gel spin coating process and different types of DSSCs were fabricated using two different classes of natural dyes, xanthenes, anthocyanins and a mixed-dye with equal proportion mixture of xanthenes and anthocyanins. The ultraviolet-visible (UV-Vis.) absorbance spectra were compared with performances of the cells. Efficiency of fabricated cells and cell characteristics were found to be related with absorption spectra of dyes.

Key words: absorption spectra, dye-sensitized solar cell, efficiency, natural dyes, ZnO nanorods.

Introduction

Conversion of solar-energy and electric-energy storage are becoming most import techniques towards issues on energy crisis and sustainable use. For the solar-energy conversion, as mostly by the form of crystalline solar cell, DSSCs with nanocrystalline ceramics, dye molecules, and electrolytes are recently developed for light harvesting (Gratzel 2003,Tennakone *et al* 1996). DSSCs are a promising low cost, green energy source (Hao *et al.* 2006, Amao *et al.* 2004). A power conversion efficiency of 11.18% has been achieved (Gratzel 2003). DSSC is a device for the conversion of visible light into electricity.

Solar cell production has grown at about 30% per annum over the past 15 years. In recent years, great attention has been paid to DSSCs due to their low fabrication cost as a viable alternative technology for renewable energy (Gratzel 2003). It has attracted much attention due to its environment friendly nature, high efficiencies and potentially low production costs. Organic dyes have been intensively investigated due to their potential use in various low-cost, large area DSSC applications. (Pradhan 2007, Pradhan *et al.* 2004)

Normally Titanium dioxide (TiO_2) nanostructures are used to fabricate DSSC. However, ZnO has shown a great deal of research interest in DSSCs due to some of its fascinating properties. ZnO is often utilized as a photo anode material in DSSCs due to its properties such as large exciton binding energy, wide direct band gap of 3.27 eV, which is generally used in organic solar cells (Gratzel 2003,Tennakone *et al.* 1996).

ZnO is also highly transparent, which allows for greater light penetration. Finally, 1-D single crystal structure formation is possible with ZnO, enabling a higher surface-to-volume ratio for greater dye loading.

To increase the conversion efficiency of ZnO nanorod-based DSSCs, it would be desirable to eliminate the interface between Indium doped Tin oxide (ITO) and the ZnO nanorods (Pradhan *et al.* 2004, *Tsubomura et al.*1976, Terahara *et al.* 1990 and Bandhopadhyay *et al.* 2003). Some researchers (Chen *et al* 2008) have recently taken up this concept by growing ZnO nanorods on a ZnO film using a two-step method. In this work ZnO nanorods were grown on an ITO coated glass using sol-gel spin coating technique.

The absorption spectrum of the dye and the anchorage of the dye to the surface of ZnO are important parameters determining the efficiency of the cell. Generally, transition metal coordination compounds (ruthenium poly-pyridyl complexes) are used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer (Duffy *et al.* 2000, Gratzel 2001 & Law *et al.* 2005). However, ruthenium polypyridyl complexes contain a heavy metal, which is undesirable from point of view of the environmental aspects and high cost (Amao & Komori 2004). Moreover, the process to synthesize the complexes is complicated and costly. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency (Pradhan *et al.* 2007, Polo and Iha 2006, Garcia *et al.* 2003, Smested 1998 and Cherapy *et al.* 1997). The advantages of natural dyes include their availability and low cost (Cherapy *et al.* 1997). The sensitization of wide bandgap semiconductors using natural pigments is usually ascribed to anthocyanins. This makes electron transfer from the anthocyanins molecule to the conduction band of ZnO (Garcia *et al.* 2003). As reported (Pradhan *et al.* 2007, Cherapy *et al.* 1997), anthocyanins from various plants gave different sensitizing performances. However, there is no acceptable explanation behind these results, so far. A natural organic dye, pomegranate juice (*Punica Granatum L.*) is a common source of anthocyanin and is commonly used for fabricating DSSCs.

Rose Bengal dye is one of the best photo sensitizers for ZnO photoanode to date and is much cheaper than Ru-complex dyes (Nazeeruddin *et al.* 1993). It is in xanthene class which absorbs wide spectrum of solar energy and energetically matches the ZnO and usual KI-I_2 redox couple for DSSCs applications (Duffy *et al.* 2000).

The performance of DSSCs using the mixed xanthene dyes was also investigated by some earlier workers (Gerischer *et al.* 1968, Watanabe *et al.* 1976). Two xanthene having different absorption characteristics would give even more synergistic effect compared to the mixed xanthene–chlorophyll dye was reported (Pradhan and Bandhopadhyay 2004). This is because xanthene has advantages over chlorophyll as DSSC sensitizer (Cherepy *et al.* 1997). Two kinds of dyes, namely, metal-organic complexes (e.g., Ru-complexes) (Frank 2005) and metal-free organic dyes, (Gerischer *et al.* 1968, Watanabe *et al.* 1976, Islam *et al.* 2001) have been widely used as sensitizers of DSSCs. Organic dyes have several advantages as photo sensitizers for DSSCs: (1) Larger absorption coefficients than metal-complex photo sensitizers; (2) variety in their structures provides possibilities for molecular design, e.g., the introduction of substituent, and thus allows for easy control of their absorption spectra; (3) inexpensive because they do not contain noble metals like ruthenium. This reduces the overall cost of the cell production.

In this study, a natural organic dye of class Anthocyanin, pomegranate juice was investigated in fabricating ZnO nanorods based DSSCs as these dyes are abundant in tropical countries (Nazeeruddin *et al.* 1993) which resulted in low fabrication cost. Another cell is fabricated with Xanthene class of dye, Rose Bengal, and a third cell was fabricated with a mixed Dye prepared by mixing equal proportions of Rose Bengal and Pomegranate juice. Finally, the qualities of the fabricated cells were investigated in terms of standard cell parameters including its conversion efficiency. The effects of dyes are discussed in terms of their UV-Vis. absorption spectra.

Methodology

ZnO nanorods were synthesized using sol-gel method and fabricated using spin coating technique. Spin-coating is a simple method for preparing znO nanoseed from zinc acetate solution. In this process, we prepared 5 mM solution of Zinc acetate dehydrate $(CH_3COO)_2Zn, 2H_2O$, (98% Merck) was prepared with methanol. The solution was spun on indium tin oxide (ITO)-coated glass substrates at 1000 rpm for 30s. The zinc acetate solution was spread on a rotating substrate (Pradhan *et al.* 2007, Cherepy *et al.* 1997). The substrates were heated to 350 ^{0}C in conventional oven for 30 min to yield layers of ZnO islands with their (100) plane parallel to the substrate surface. After evaporation of solvent, a thin ZnO film was formed. Repetition of the above process 5 to 7 times was carried out to control the thickness of the film. Concentration of the solution and spinning speed of the substrate also played important roles in adjusting the thickness of the fabricated film. The counter electrode (cathode) was prepared on another ITO coated glass by using carbon dust.

Characterization of dye and Dye Deposition

The device was then immersed in a solution of sensitized dye for 24 hours to allow the dye molecules to form covalent bond to the surface of the ZnO. The samples were then rinsed with ethanol to remove excess dye on the surface and air-dried at room temperature. The absorption spectra of dyes were recorded using a UV–Vis spectrophotometer (Perkin Elmer Lamda-35 model UV-Vis).

DSSC assembling

DSSCs were assembled following the procedure described in the literature (Pradhan *et al.* 2007). The carbon dust coated counter electrode was placed on the top so that the conductive side of the counter electrode faces the ZnO film. The iodide based solution as the liquid electrolyte (0.5M potassium iodide mixed with 0.05M iodine in water-free ethylene glycol) was placed at the edges of the plates. The liquid was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together.

Device Characterization and Measurement

Apparatus setup

Keithley model 2400 digital source pico-ammeter was used to measure the dark and illuminated *I-V characteristics* of the DSSC under white light illumination (Xenon-lamp) conditions for the efficiency calculation. The position of the light source was adjusted such that the light intensity was 100 mW/cm^2 (equivalent of one sun) at AM 1.5. The current-voltage characteristics of DSSCs under various light intensities were obtained.

Characteristics of dye-sensitized solar cells

The current–voltage characteristics of a cell in the dark and under illumination permit an evaluation of most of its photovoltaic performances as well as its electric behavior (Rostalski & Meissner 2000).

The short circuit current (I_{sc}) is the one which crosses the cell at zero applied voltage and it is a function of illumination. Charges travel under an internal potential difference typically equal to open circuit voltage (V_{oc}).

The V_{oc} is measured when current in the cell is 0, corresponding to almost flat valence and conduction bands; I_{max} and V_{max} values are defined in order to maximize the power $|I_{max} \times V_{max}|$. This is the maximum power P_{max} delivered by the cell. The fill factor FF is the ratio of the maximum power to product of short circuit current and open circuit voltage.

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

The external photovoltaic yield or efficiency ç is defined as the ratio of the maximum electric power extracted to the illumination times the surface area, i.e. P_{in} of the cell:

$$\eta = \frac{[V_{oc} \times I_{sc} \times FF]}{[P_{in}]} \times 100\% \quad \dots (2)$$

(It is often expressed as a percentage). Conversion yield is the key parameter as concerns cells productivity (Rostalski and Meissner 2000).

The equivalent circuit model of DSSC

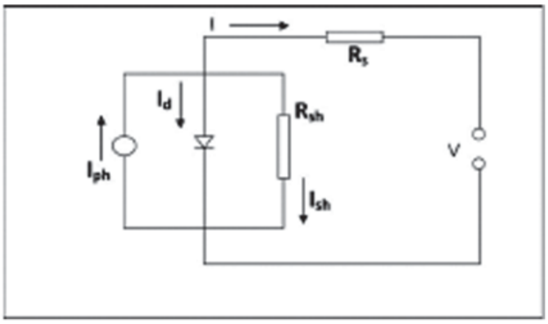

Fig. 1 Equivalent Circuit Diagram of DSSC

A solar cell is generally characterized using the equiv lent circuit of the single diode model as shown in Figure 1 and the relation between the current *I* and the voltage *V* is given by

$$I = I_{ph} - I_s\left[exp\left\{\frac{q(V + R_s I)}{A k_B T}\right\} - 1\right] - \frac{V + R_s I}{R_{sh}} \quad \dots (3)$$

where I_{ph}, I_s, R_s, R_{sh}, q, A, k_B, and T are the photocurrent, the saturation current of the diode, the series resistance, the shunt resistance, the electron charge, the ideality factor, the Boltzmann constant, and absolute temperature, respectively.

Results and Discussion

Structure characterization

The morphology of the samples was observed using a scanning electron microscope (SEM) with a field emission gun operating at 200 kV. Figure 2a displays ZnO nanowire arrays in a wide surface area. The nanorods have an average length of 600 nm, diameter ranging from 100 to 200nm and they are mostly vertically aligned with the substrate having hexagonal shapes. Figure 2b shows hexagonal shapes of ZnO. The thickness of ZnO film was around ~2 ìm.

The nanowires, which make barrier free contact with the substrates, exhibit resistivity around 0.3 to 2.0 Wcm along the long axis (Islam *et al.* 2001). The nanowire used in the present work had a resistivity 0.7 Wcm at 0V. Due to absence of interfaces in nanowires, resistivity of a nanowire should be lower than nanoparticle thin films. Moreover, conductivity in the nanowire arrays increases by 5 to 20% when they are soaked in standard DSSC electrolytes (Islam *et al.* 2001).

In general, the energy conversion efficiency of ZnO based DSSCs is lower than that of TiO_2 based DSSCs (Fran 2005, Nazeeruddin *et al* 1993, Islam *et al.* 2001). However, due to the barrier free contact, ZnO nanowire is expected to give higher efficiency. Because only about 4% of the solar spectrum falls in the UV region, ZnO semiconductor absorbs solar radiation while sensitized by natural dye molecules with absorption spectra at visible region.

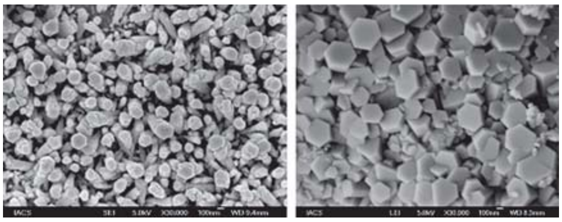

Fig. 2. Scanning electron microscopic (SEM) micrographs of ZnO nanorod used in the dye-sensitized solar cell

\Anthocyanin dyes present in Pomegranate Fruits are responsible for absorption of solar energy Miguel *et al.* 2004). Anthocyanin dye is responsible for several colors in the red–blue range depending on pH value. The red anthocyanin absorbs at 530 nm (band gap 2.3 eV), whereas, Rose Bengal has got a Xanthene class of dye with a band gap 1.9 eV and maximum absorption peak at 555 nm.

After absorbing photon energy from the illuminated white light, the dye molecules in the DSSCs become excited and inject electrons to the ZnO nanowires (Fig. 3). Due to favorable energy difference, electron transfer occurs between the lowest unoccupied molecular orbital (LUMO) of the dye and the conduction band of ZnO. The photogenerated electrons percolate rapidly through the ZnO nanowire and are collected by the conducting glass support. The highest occupied molecular orbital (HOMO) of the dye is energetically lower than the redox potential, E_{redox} of the iodine/triiodide couple. The energy difference provides the driving force for hole injection into the electrolyte. Recombination of charge carrier is also minimized in such devices since transport of only one type of carrier (electron, in general) is energetically possible from the dye to the semiconductor. For Rose Bengal dye (Xanthenes), the energy difference is 1.9 eV (Pradhan *et al.* 2004) and for pomegranate (Anthocyanins) the energy difference is 2.3 eV (Miguel *et al.* 2004).

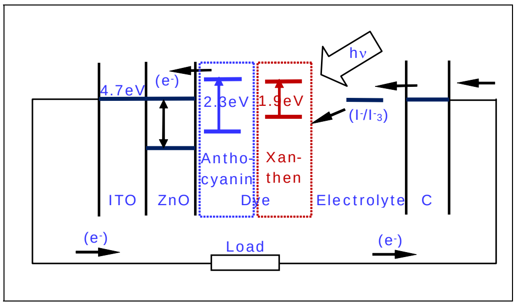

Fig. 3. Schematic band diagram showing the working principle of DSSC with various dyes

Characterization of dyes

Three organic dyes which are commonly used to sensitize the semiconductor layer in DSSC are Rose Bengal, Pomegranate and Mixed Dye having absorption peak at 555, 525, and 545 nm, respectively as shown in Fig. 4. These dyes suffer from the fact that individually they absorb very small portion of the visible spectrum of solar radiations giving rise to a low efficiency of DSSCs. The peak of the absorption spectra of the dyes are in tune with HOMO-LUMO energy difference of Xanthene and Anthocyanin class of dye.

Since no single dye can perform efficiently in the entire visible spectrum, the present work is focused on the performance study of I-V curve of DSSCs with various dyes having broadband absorption in the visible spectrum for efficient harvesting of light by DSSCs. The Rose Bengal dye absorbs a larger fraction of the solar spectrum in the visible region 460–650 nm. The Rose Bengal dye has been used to sensitize ZnO electrode of the DSSCs. On the other hand Pomegranate is a natural dye with wider absorption peak at lower wavelength range of solar spectrum. The spectrum of mixed dye shows even wider absorption band and is expected to harvest more solar energy.

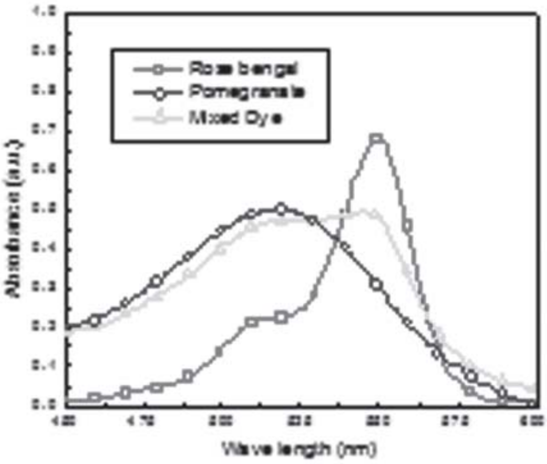

Fig. 4. Absorption spectra of Rose Bengal, Pomegranate and Mixed dye

We have recorded *I-V* characteristics of ZnO nanorods based DSSCs using Rose Bengal, Pomegranate (*Punica Granatum*) and Mixed dye with equal proportion mixture of these two, with varied external resistances under illumination.

Figure 4 shows the current voltage curves of various dyes based DSSCs. The Rose Bengal dye shows highest short circuit current whereas Pomegranate has lower value of both open circuit voltage and short circuit current. However, the mixed dye showed highest open circuit voltage with appreciable short circuit current.

Photovoltaic properties

The V_{oc}, I_{sc}, voltage at maximum power (V_{max}), current at maximum power (I_{max}), values of DSSC cells with three different dyes were calculated from Figure 5 and fitted with the Equation 3 for one diode equivalent circuit model (Fig. 1) by Newton-Raphson's method. Results of Curve fitting are given in Table-I.

The parasitic resistances (series and shunt) of DSSCs are important parameters that affect their efficiency. The resulting parasitic resistances, series (R_s) and shunt resistance (R_{sh}) were evaluated from these results. Pomegranate has high series resistance, whereas using mixed dye subsequent reduction in series resistance was obtained, which results in substantial improvement in cell performance. From the data of Table-I, it was confirmed that for all kinds of cells, higher the shunt resistance, the efficiency is lowered and efficiency raises with lower series resistances. The fill factor (FF) for all the cells using different dyes are also evaluated from the I-V characteristics using equation (1) and finally the energy conversion efficiency (h) is calculated using equation (2). All these results are presented in Table-I.

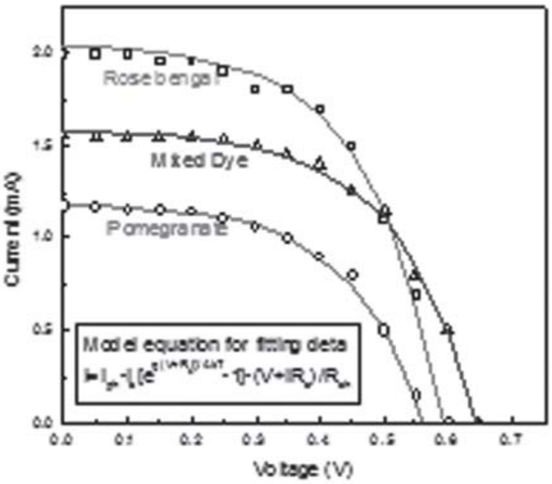

Fig. 5. Current-voltage curves of various dyes based DSSC

All cell parameters like Ideality Factor (A), Fill factor (FF) and Energy conversion efficiency (h) of ZnO-nanorod-based DSSCs with different dyes are calculated and presented in Table-I where values are calculated from current voltage curves of DSSC cells fabricated with various dyes.

Table I. Solar cell parameters of the three DSSCs

ZnO DSSC Dyes	V_{oc} (V)	I_{sc} (mA)	I_s (µA)	R_s (Ω)	R_{sh} (Ω)	*A*	*FF*	η (%)
Rose Bengal	0.6	2.1	13.26	0.00308	3461	4.55	0.49	1.56
Pome-granate	0.56	1.18	9.88	0.00489	5011	4.57	0.56	1.01
Mixed Dye	0.65	1.57	7.96	0.00171	3934	4.73	0.54	1.41

The Rose Bengal dye shows highest efficiency and lowest fill factor, whereas Pomegranate shows lowest efficiency and highest fill factor. Though the mixed dye has an intermediate value of efficiency and fill factor, its values are very close to that of Rose Bengal. So, by mixing two kinds of dyes we achieved very good efficiency, which may be due to exploitation of wider band of energy in the solar spectrum as found out by the UV-Vis. spectroscopic results of the mixed dye. This improvement in efficiency of the mixed dye is due to the improvement in ideality factor. Ideality factor indicates perfectness of the diode in the equivalent circuit, and it is 1.0 for a perfect diode. In our observation an improvement in ideality factor was observed, 4.73 for mixed dye, compared to 4.55 and 4.57 of pure dyes.

ZnO nanorod based DSSC solar cells were fabricated on ITO coated glass substrate and the cell performance of ZnO-based DSSCs was found out for two types of dyes and also for their mixture. The dyes differ in their absorption spectra and absorb sunlight in different frequency range. The mixed dye with larger band of frequency spectrum shows improvement in efficiency than the average efficiency of the two dyes. This improvement in efficiency of the mixed dye is due to the improvement in ideality factor.

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