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Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Optimizing the Preparation Parameters

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1-1 Introduction

With the ever increasing population of the earth, the demand for energy becomes the most important problem for the next 50 years. Most energy is provided at present by burning fossil fuel, but the extensive usage of fossil fuel produces also a greatly increased concentration of atmospheric CO_2 that causes global warming. A search for a clean and sustainable source of energy free of carbon has therefore become an important issue for scientists. The most obvious source is the sun [1]. Solar energy is expected to play a crucial role as a future energy source. More solar energy strikes the earth in one hour (4.3×10^{20} J/hour) than all the energy consumed on the earth in a year (4.1×10^{20} J/year) [2] Solar energy provides clean abundant energy and is therefore an excellent candidate for a future environmentally friendly energy source.

There are various types of solar cells that convert sunlight into electrical energy such as silicon solar cell and thin film solar cell. For example, dye sensitized solar cell (DSSC). The DSSC is the third generation of solar cell which has been developed by O'Regan and Gratzel in 1991 [3] using nanocrystalline semiconductor oxide material sensitized by a ruthenium (Ru) dye enabled a paradigm shift in the field of solar energy conversion technology [4]. Due to the pioneer work of Gratzel, the DSSC is also known as Gratzel cell [5].

Unlike the common solid state solar cells based on crystalline silicon, the DSSC does not depend on the principle of a p-n junction for its basic operation [6]. The DSSC uses dye molecules adsorbed on the nanocrystalline oxide semiconductors such as TiO_2 to collect sunlight. Therefore the light absorption (by dyes) and charge collection processes (by semiconductors) are separated, mimicking the natural light harvest in photosynthesis. However, DSSC has become one of the important and promising technologies in photovoltaic field [7], due to low material cost, simple fabrication process, high energy conversion efficiency as compared to other thin-film solar cell technologies and low toxicity to the environment [8]. DSSC consists of four main components: a nanostructured semiconductor (typically TiO_2), a dye-sensitizer to absorb visible light, an electrolyte (typically contain iodide and triiodide) and counter electrode (typically Pt) [9]. Different parameters affect efficiency of the DSSCs: types of materials used as electrolyte, dye and electric contact, and synthesis method used to obtain these materials [7].

The DSSC can be classified as a photoelectrochemical (PEC) solar cell due to its utilization of photons, charges, and electrolyte for its basic operation [6]. Typically, high power conversion efficiencies (η) of more than 11 % have been achieved by using ruthenium complex and acetonitrile based electrolytes [10].

The advantages of DSSC are that it can be engineered into flexible sheets, low cost of sensitization material production, ease of fabrication and low process temperature. The performance of the DSSC is highly dependent on the sensitizer dye and wide bandgap material such as TiO_2, ZnO and Nb_2O_5 [11].

1-2 Literature Review

In **1991,** Oregan and Gratzel, fabricated DSSC with a suitable thick TiO_2-film immersed with a solution of Ruthunium dye to sensitize the substrate for collecting the light. Better current density (greater than 12 mA cm^{-2}) was obtained. The energy conversion efficiency was 7.1-7.9 % in simulated solar light and 12 % in diffuse daylight [12].

In **1997**, Usami reported a theoretical study of application of multiple scattering of light to a dye sensitized nanocrystalline photoelectrochemical cell. The cell effectively confines incident light in the thinner dye sensitized film by multiple scattering from dispersed TiO_2 particles at the bottom and total reflection between the inserted TiO_2 film and the glass substrate at surface. Under optimal scattering conditions, it was found that the backscattered intensity is maximized when the backscattering angle is equal to the critical angle of reflection at the surface. The optical confinement is also effective for long wavelength light [13].

In **1999**, Tennakone et al., prepared dye sensitized solar cell (DSSC) from a porous film consisting of a mixture of tin and zinc oxides sensitized with a ruthenium bipyridyl complex suppresses recombination of the photo generated electrons and dye cations. It was found that short circuit photocurrent was 22.8 mA/cm^2, open circuit voltage was 670 mV and conversion efficiency was 8 % in direct sunlight (900 W/m^2) [14].

In **2001**, Lindstrom et al., fabricated the DSSCs by new method, the method was summarized with manufacturing a nanostructured porous layer of a semiconductor material at room temperature. The porous layer is pressed on a conducting glass or plastic substrate. The method compresses the particle layer to form a mechanically stable, electrically conducting, porous nanostructured film. Overall, solar to electric conversion efficiencies of up to 5.2 % at 1 sun using plastic substrates have been obtained [15].

In **2002**, Boschloo et al., prepared dye sensitized solar cell (DSSC) with using Degussa P25 TiO_2 powder, red dye ($Ru(dcbpy)_2(SCN)_2$), black dye ($Ru(tcterpy)(SCN)_3$) and an electrolyte were tested using standard photoelectrochemical techniques. It was found that the average overall efficiency of small open cells sensitized with the red dye on plastic substrates was 4.5 % (100 W m^{-2}). In a direct comparison, red and black dye gave about the same efficiencies [16].

In **2003**, Wang et al., fabricated and enhanced performance of dye sensitized solar cells (DSSCs) by using Co-grafting amphiphilic sensitizer. The results indicated that enhanced in short circuit photocurrent was 15.2 mA cm^{-2}, an open circuit photovoltage was 764 mV, and a total power conversion efficiency was 7.8 % under simulated full sunlight when DSSCs containing Co-grafting [17].

In **2004**, Wang et al., studied the influence of titania photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell. It was found that the energy conversion efficiency of N719 dye-sensitized solar cell has improved significantly from 7.6 to 9.8 % by tuning the film structure from monolayer to multilayer [18].

In **2006**, Bandara and Weerasinghe, designed DSSC with high efficiency using coupled dye mixtures [Ru(2,2-bpy-4,4'-dicarboxylic acid)$(NCS)_2$] and [Ru(4,4',4"-tricarboxy-2,2;6,2"-terpy)$(NCS)_3$]. It was found that short circuit current density (J_{SC}) of 10.2 mA/cm^2, conversion efficiency (η) of 2.8 and incident photon to current conversion efficiency (IPCE) 50 % while broadening the spectral sensitivity of the cell for multiple dye system. When single dye Ru(4,4-bis(carboxy)-bpy)$_2$$(NCS)_2$] or [Ru(2,2',2"-$(COOH)_3$-terpy)$(NCS)_3$] was used, cell efficiencies of 1.7 and 1.2 were observed respectively [19].

In **2006**, Hore et al., studied the influence of thin TiO_2 layer with different scattering layer on the efficiency of DSSCs. It was found that J_{SC} increased due to inclusion of scattering layers [20].

In **2007**, Lee et al., fabricated dye sensitized solar cells (DSSCs) using TiO_2 coated multi-wall carbon nanotubes (TiO_2-CNTs). It was found that the TiO_2-CNTs content (0.1 weight %), the cell showed increase ~50 % in conversion efficiency, which is attributed to the increase in short circuit current density (J_{SC}). The enhancement in J_{SC} occurs due to improvement in interconnectivity between the TiO_2 particles and the TiO_2-CNTs in the porous TiO_2 film [21].

In **2008**, Chou et al., improved performance DSSC by using electrodes that consist of TiO_2 with addition of indium doped tin oxide (ITO) or fluorine-doped tin oxide (FTO) nanoparticles [22].

In **2009**, Sakurai et al., fabricated and enhanced the efficiency DSSC by using ClO_4^- -poly (3,4-ethylenedioxythiophene)/TiO_2/FTO (ClO_4–-PEDOT/TiO_2/FTO) counter electrode (CE) in dye sensitized solar cells (DSSCs) is fabricated by using an electrochemical deposition method. It was found that the current-voltage (I-V) measurement reveals that the photocurrent conversion efficiency (η), fill factor (FF) and short-circuit current density (J_{SC}) of DSSCs with a ClO_4^--PEDOT/TiO_2/FTO CE increased compared to DSSCs without ClO_4^--PEDOT/TiO_2/FTO CE. The enhanced performance of the DSSCs is attributed to the higher J_{SC} arising from the increase of active surface area of ClO_4– -PEDOT/TiO_2/FTO CE [23].

In **2009**, Huynh et al., improved DSSCs performance by using TiO_2 thin film prepared by doctor-blade method. It was found that the dye sensitize solar cells prepared with TiO_2 thin film shows its superior photovoltaic performance at air mass 1.5 (AM 1.5), open circuit voltage (V_{OC}) was 0.77 V, J_{SC} was 18.2 mA/cm^2, FF was 0.50 and efficiency (η) was 7.0 % [24].

In **2010**, Bazargan et al., fabricated flexible DSSCs using a new type counter electrode which prepared with an industrial flexible copper (Cu) sheet as substrate and graphite as the catalytic material which was sprayed by sprayed method. The results indicates that DSSCs fabricated with new type CE show higher solar to electricity conversion efficiency. The respective values are 5.29 % and 3.38 % for the graphite/ITO polymer based devices [25].

In **2010**, Lee and Kang, studied the properties of nanoporous structured TiO_2 and its application to dye-sensitized solar cells (DSSCs). From the results they found that the energy conversion efficiency (η) of the DSSC prepared from nanoporous structured TiO_2 was approximately 8.71 % with the N719 dye under 100 $mWcm^{-2}$ simulated light [26].

In **2011**, Xia Wu et al., prepared TiO_2 nanosheets films with various thicknesses (5-20 µm) by Doctor-Blade technique and they studied the effect of film thickness on the performance of dye sensitized solar cells (DSSCs) by I -V characterization. They showed that the optimized DSSCs performance was 8.39 % when 15 µm [27].

In **2011**, Tsai et al., enhanced the efficiency DSSCs by using Graphene-TiO_2 composites as working electrode. It was found that the increasing of the graphene content leads to increase the amount of dye absorption [28].

In **2012**, Lee et al., enhanced the efficiency of dye-sensitized solar cells (DSSCs) by combining TiO_2 nanotubes (TNTs) and nanoparticles. The incident photocurrent conversion efficiency was measured using a solar simulator and it was found to be (100 mW/cm^2). It was found also that DSSCs based on TNT/TiO_2 nanoparticle hybrids showed better photovoltaic performance than cells made purely of TiO_2 [29].

In **2012**, Ole et al., fabricated DSSCs based on photoelectrodes synthesized via Horizontal Vapor Phase Crystal (HVPC) Growth Technique. Nanostructured TiO_2 was first synthesized on glass substrates at growth temperatures of 1000 °C, 1100 °C, and 1200 °C with varying substrate distance from the bulk powder. FTO was used to deposit nanostructured TiO_2 for the photoelectrodes of the DSSCs employing the optimum substrate distance identified by SEM analysis. Bixin dye extracted from Annatto was utilized as a low-cost sensitizer and a graphite coated FTO as counter-electrode. All the DSSCs with photoelectrode fabricated by HVPC growth technique achieved a relatively large open-circuit voltage (V_{OC}) of 387 mV, 427 mV, and 412 mV for growth temperature of 1000 °C, 1100 °C, and 1200 °C respectively [30].

In **2012**, Karthick et al., prepared TiO_2 pastes from commercial P25 titanium oxide powder (sample X) and titanium isopropoxide (sample Z) using a hydrothermal technique and also fabricated DSSCs. FTO glass is used as substrate for deposition of the pastes. The coated films were sintered at 500 ºC for 30 minute and characterized by X-ray diffraction (XRD), fourier transform infrared (FTIR), ultraviolet visible (UV-Vis), scanning electron microscope (SEM), transmission electron microscope (TEM) and IV studies. XRD results confirmed that both of anatase and rutile phase were found in the film from sample X but only anatase phase were formed from sample Z. The lattice parameters of sample X is a = 3.789 Å and c = 9.526 Å and those of sample Z is a = 3.786 Å and c = 9.508 Å. Also, it was found FT-IR studies showed that there is no precursor residue present in both the sample after sintering. The UV-Vis spectrum indicates the amount of dye adsorbed on TiO_2 particle. It was found that the short circuit current (J_{SC}), open circuit voltage (V_{OC}) and conversion efficiency (η) are 11.34 mA/cm^2, 0.7111 V and 5.7 % respectively, which is high for DSSC prepared by using sample Z compared to sample X [31].

In **2013**, Guo et al., prepared and enhanced the properties of DSSCs by using differing amounts of silver nanoparticles (Ag NPs) on TiO_2. The results indicated that J_{SC} was 10.19 mA cm^{-2}, V_{OC} was 698 mV and photoelectric conversion efficiency was 5.33 % when the Ag NPs addition was 0.15 wt % [32].

In **2013**, Oladiran and Olabisi, fabricated DSSC with using FTO glass as the substrate with copper metal attached to the surface, eosin blue as sensitize, lemon juice as electrolyte and ZnO nanoparticles as photoelectrode. The nanostructured ZnO was synthesized by precipitating Zn nitrate hexahydrate with NaOH which was characterized structurally using XRD and optically with a UV-Vis Spectrophotometer. It was found that the DSSC has fill factor was 0.85 and efficiency was 0.15 % [33].

In **2014**, Deepak et al., fabricated DSSCs module by spray pyrolysis deposition (SPD) method of a TiO_2 colloid having similar to 10 nm sized TiO_2 nanoparticles. It was shown that this the process was first optimized for cell level fabrication, and the parameters (mainly the thickness) obtained from the study were subsequently used for module level fabrication. It was found also that the best efficiency obtained at the cell level (area 0.2 cm^2 and thickness of 12 mm) was 7.79 % and that for the (12 cm × 12 cm) module was 3.2 % [34].

In **2014**, Di Gu et al., studied the effect of addition of the suitable molecular weight of polyethylene glycol (PEG) of DSSC anode on its efficiency. It was found that when adding PEG of molecular weight 2000, the TiO_2 thin film electrode has the best performance, subsequently, the DSSC enhancement performance [35].

In 2014, Hammadi and Naji, studied the effect of dye concentration and added acid to the dye solution on optical properties of hibiscus sabdariffa organic dye used in the dye-sensitized solar cell. The results showed that the acidic environment of the Hibiscus sabdariffa dye solved in acetone has an important effect on the spectral properties of such dye. Adding acid to the dye solution caused to decrease its absorbance in the range 400-800 nm and noticeable decrease was shown in the range 550-700 nm when the concentration of the dye got higher [36].

In **2015**, Gomesh et al., fabricated DSSC with the usage of recycled materials and organic dye such as graphite from batteries and organic dye from rose extract. The study focused on electrical performance and characteristic of the fabricated TiO_2 solar cell based on the graphite coating thickness. The results were investigated in terms of fill factors, solar cells efficiency and UV-Vis absorption. Result showed that thinner layer of graphite coating has good potential as an alternative counter electrode material [37].

In **2015**, Uddin et al., prepared and studied the properties of DSSC using natural dye extract from red amaranth as sensitizer. It was found the best light to electricity conversion efficiency was obtained when sensitization time of electrode was 30 minutes and dyes were extracted by acetone in crude form. Subsequently, the DSSC generated maximum voltage 0.492 V, short circuit current density 0.78 mA/cm^2 and cell efficiency 0.22 % [38].

In **2015**, Sedghi and Miankushk, studied the effect of thickness of TiO_2 electrodes on the performance of dye-sensitized solar cells. TiO_2 electrodes were characterized by SEM, optical microscope (OM), FTIR, thermal gravimetric analysis (TGA), and also cell performance was measured by a solar light simulator at an intensity of 1000 $W.m^{-2}$. It was found that increasing the thickness of the TiO_2 films led to absorption of the N719 dye increased, so that η of 7.51 % was obtained [39].

In **2015**, Hussein, fabricated three types of DSSC [pure TiO_2 cell (TiO_2 only), bare TiO_2 cell (TiO_2 sensitized by Curcumin dye) and treated TiO_2 cell (TiO_2 HCl $TiCl_4$ sensitized by Curcumin dye)] and improved performance of dye sensitized solar cell (DSSC) by utilization natural Curcumin dye extracted from Curcuma longa plant (Turmeric) as photosensitizer. It was found that the bare TiO_2 cell has achieved the highest power conversion efficiency with value of 1.15 % in comparison with (treated and pure) TiO_2 cells [40].

In **2016**, Li et al., fabricated flexible DSSC modules on plastic substrates. It was shown that the conversion efficiency was maximum (~ 30 %) for the flexible DSSC modules with series connection [41].

In **2016**, Pirhadi et al., fabricated dye sensitized solar cells (DSSCs) with single layer and double layers photoanode. It was found that the DSSCs with double layers photoanode resulted higher efficiency compared to DSSCs with single layer photoanode. The photovoltaic characteristics of DSSCs with double layers photoanode were 734 mV, 13.16 mA/cm^2, 62 % and 5.96 % for V_{OC}, J_{SC}, FF and efficiency respectively [42].

In **2016**, Jaber et al., fabricated and enhanced the performance of DSSC by using gold nanoparticles (Au NPs). Au NPs prepared by laser ablation in liquid (PLAL) method at 750 mJ energy and 90 pulses. They have been added to $[RuL_2(NCS)_2]$: 2TBA (L=2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA=tetra-*n*-butylammonium) (N719) dye to form (Au-N719) mixture. TiO_2 paste was deposited on FTO substrates and immersion in a mixture dye and Au NPs. The UV-Vis data show high absorbance of Au NPs+N719 dye compared to N719 dye only. Scanning electron microscope shows spherical Au NPs with particle size about (50-60) nm. The results indicated that the relative increase of short circuit current density and open circuit voltage after adding Au NPs was about 76 % and 6.7 % respectively. The results indicated that the total photon to current energy conversion efficiency for the standard DSSC is 1.75 while its 2.8 of the enhanced DSSC with gold NPs. The maximum enhancement is about 60 % under illumination (105 mW cm^{-2}) [43].

In 2016, Salman and Agool, prepared ZnO nanoparticles by laser ablation technique and fabricated dye-sensitized solar cell (DSSC) from ZnO nanoparticles using electrostatic deposition technique. From the results, they found that the ZnO nanoparticle had crystalline wurtzite phase. Also, Transmission electron microscopy (TEM) image illustrated that the ZnO nanoparticles were spherical in shape with an average size of about 37 nm**.** The fabricated ZnO-DSSC had a fill factor of 0.29 and conversion efficiency of 0.0016 % [44].

To the best of our knowledge, no previous studies have been conducted about the effect of adding (Au NPs) to (Z907 dye) (RuLL'$(NCS)_2$ (L=2,2'-bipyridyl-4,4'-dicarboxylic acid;L'=4,4'-dinonyl-2,2'-bipyridine) and dye mixtures on the efficiency of DSSC.

1-3 Aim of the work

- ❖ Fabrication of dye sensitized solar cells (DSSCs) and studying their properties.
- ❖ Studying the effect of titanium thickness on DSSC efficiency.
- ❖ Studying the effect of adding Au NPs on DSSC efficiency.
- ❖ Studying the effect of dyes mix on DSSC efficiency.