Imine-linked receptors decorated ZnO-based dye-sensitized solar cells

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Abstract. This study reports the synthesis, characterization and photophysical properties of imine-linked receptors decorated ZnO nanoparticles using wet precipitation method. Initially, polymer dye 3 was synthesized using condensation reaction between 2-furancarboxaldehyde 1 and polyethylenimine 2. The decoration of imine-linked receptors on ZnO nanoparticles (sample A) was characterized and investigated by X-ray diffraction, scanning electron microscope and dynamic light scattering spectroscopic studies. Further, polymer dye 3 was added to ruthenium chloride (RuCl_3) to form a polymer–ruthenium-based composite dye-capped ZnO nanoparticles (sample B). The optical properties of sample A were evaluated by fluorescence and UV–Vis spectroscopy. The samples A and B were further processed to dye-sensitized solar cells using wet precipitation method. The results of observations revealed that the addition of ruthenium–polymer dye molecules increased the light harvesting capacity of ZnO-based DSSCs. A maximum solar power to electricity conversion efficiency (η) of 3.83% was recorded for sample B-based DSSCs with ruthenium–metal complex dye as a good photosensitizer. The recorded photovoltaic efficiency of sample B-based DSSCs was enhanced by 1.36% compared to sample A-based DSSCs.

Keywords. Imine-linked receptors; ruthenium–metal complex; ZnO nanoparticles; dye-sensitized solar cell.

1. Introduction

Continuously, the increasing demand of energy and limited natural fuel resources have motivated the scientists for searching viable renewable energy resources across the world. The design and modulation of dye-sensitized solar cells (DSSCs) for converting solar power into electricity boosts the attention of researchers during last decade. The conventional silicon solar cells exhibited power conversion efficiencies from 10 to 34% [1]. Despite good photovoltaic performances of silicon-based solar cells, their applicability is limited due to high costs of complicated fabrication designs. DSSCs based on polymers have been proposed as a cost-effective alternative to the conventional silicon solar cells, because of their excellent optical and photovoltaic properties, and ease of synthesis processes. They have high photons power to electric conversion efficiency (11–12% under laboratory conditions), good stability and long-term reliability [2]. Polymer-based DSSCs utilize interpenetrating nanostructure based on electron-donor and electron-acceptor materials. Polymer-based DSSCs use a layer of polymer-capping agent and an inorganic semiconductor material (ZnO or TiO_2 acting as photoanode of solar cell) to convert photons energy into electricity [3–5]. The optimal light harvesting capability, high electron mobility of inorganic material

and high hole mobility of polymer material lead to most advantageous fabrication of DSSCs [6]. ZnO has been widely used in excitonic optoelectronic applications as compared to other group II–IV compound semiconductors, due to its wide bandgap (3.37 eV) nature and a high exciton binding energy of 60 meV with a stable wurtzite structure. Due to its unique and attractive features, ZnO has been used in antireflection coatings, transparent electrode layers of solar cells, light-emitting diodes, spin electronics, UV light emitters, optoelectronic sensors, etc. [7,8]. ZnO nanoparticles are capable of providing high sensitivity and excellent stability due to their high surface-to-volume (S/V) ratio. Furthermore, ZnO is environment friendly (non-toxic) and absolutely suitable for bio-applications (bio-imaging and dentistry) [9]. A number of research papers have been studied regarding the use of ruthenium–metal complexes for DSSCs [10–16]. Polymer-decorated ZnO (with imine-linked receptors and ruthenium–metal complex) in the fabrication of DSSCs has not been investigated earlier. So in this research work, imine-linked receptors decorated ZnO-based DSSCs are fabricated to enhance the light harvesting capability and overall photon energy to electric conversion efficiency. The main objective of polymer-decorated ZnO nanoparticles with imine-linked receptors (as capping agent) is to passivate the surface of ZnO nanoparticles and prevent them from aggregation. The passivation process increases the photovoltaic efficiency and overall light harvesting performance of the ZnO-based

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DSSCs. Several methodologies have been developed for the synthesis of polymer-decorated ZnO nanoparticles. Recently, DSSC photoelectric power conversion efficiencies of 11.1 and 12.3% have been reported using ruthenium and porphyrin dyes with different redox couples of iodine and cobalt for TiO_2 [17]. Yoon *et al* [18] have compared the performance of polymer dye-based solar cells with different functional groups and recorded an energy conversion efficiency of 2.32%. The synthesis methods used in the above-referred research papers are little complex and costly. Including chemical vapour deposition, hydrothermal, spray pyrolysis, sol-gel route, screen printing methods [19], the wet precipitation method is the most suitable and successful approach due to its clean, economical and eco-friendly requirements for laboratory work [20,21]. The present research work has explored the possibility to smoothly decorate the imine-linked receptors on the surface of ZnO nanoparticles.

For the present research work, the design and modulation process of ZnO-based DSSCs depends on the total surface decoration of ZnO nanoparticles with imine-linkage receptors ($-\text{NH}_2$) and ruthenium-metal complex dye acting as a good light adsorbent or sensitizer [22–24]. The polymer-based DSSCs are cheapest in cost, respond to better aggregation of ZnO nanoparticles and efficient light harvesting performances. The polymer-capped ZnO DSSCs are flexible in shape, transparent, multicoloured and perform better under sun illumination conditions than TiO_2 - and silicon-based solar cells [25–29].

2. Experimental

The following section discusses the synthesis procedure of imine-linked receptors, their decoration on ZnO nanoparticles and finally fabrication of the ZnO-based DSSCs.

2.1 Materials preparation and instrumentation

All the chemicals were purchased from a commercial supplier and used without further purification for all experiments. For the synthesis of imine-linked receptors decorated ZnO

nanoparticles, ^1H NMR and ^{13}C NMR spectra were recorded on Avance-II (Bruker) instrument. The fluorescence spectra of sensor solutions were recorded on Perkin Elmer L55 Fluorescence spectrophotometer, using 1 cm path length of quartz cells. The slit width for the excitation and emission was set at 10 nm and scan speed was maintained at 200 scans s^{-1} throughout the experiment. Scanning electron microscope (SEM) images were taken with Jeol JSM-6610LV SEM, which operated at 15 keV. The size of ZnO nanoparticles was determined by dynamic light scattering (DLS), using external probe feature of Microtrac Ultra Nanotracer Particle Size Analyzer instrument. The crystallite structure of the ZnO powder was analysed using X-ray diffraction (XRD) with a PANalytical X'PERT PRO diffractometer operated at 45 kV and 40 mA using Ni-filtered $\text{Cu K}\alpha$ radiations with a scan speed of $10^\circ \text{ min}^{-1}$ for 2θ in a range from 10 to 75. The average crystalline size of ZnO nanoparticles was estimated by Debye-Scherrer's equation using XRD analysis data [21]. For measuring photovoltaic characteristics of ZnO-based DSSCs, an ultrafine digital multimeter (Omega DMM 101) was used throughout the experiment.

2.2 Synthesis of imine-linked receptors (polymer dye 3)

Polymer dye **3** was synthesized by reaction of 2-furan-carboxaldehyde (2-FC, **1**, 1 mmol) and polyethylenimine (PEI, **2**, 2.5 mmol) in dry methanol. The solution was refluxed for 6 h. After completion of reaction, solvent was evaporated under reduced pressure and products were purified. A pale yellow product was separated out and the product was washed with methanol and finally polymer dye **3** (imine-linked receptors) was characterized with ^1H NMR, mass, IR and CHN spectroscopy. Figure 1 shows the chemical schematic for the formation of imine-linked receptors or polymer dye **3**.

A light yellow solid was obtained in 90% yield, m.p. $> 200^\circ\text{C}$; IR (KBr): ν_{max} 1665, 1530, 1240, 1225 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 8.15(brs, 4H, $\text{CH}=\text{N}$), 7.71–7.74(m, 3H, ArHs), 7.62(dd, 1H, ArH), 7.43–7.35(m, 4H, ArHs), 7.21–7.13(m, 4H, ArHs), 3.75(t, 2H, CH_2),

Figure 1. Synthesis of polymer dye **3** (imine-linked receptors).

3.65(t, 4H, CH₂), 3.42–3.80(m, 4H, CH₂), 3.17(s, 1H, NH), 3.06–2.90(m, 4H, CH₂), 2.82–2.65(m, 6H, CH₂), 2.60–2.50(m, 6H, CH₂), 2.49–2.46(m, 4H, CH₂), 2.45–2.41(m, 4H, CH₂), 2.37–2.32(m, 4H, 2 × CH₂), 1.90–1.81(m, 2H, CH₂), 1.64(s, 1H, NH), 1.62(s, 1H, NH), 1.61–1.53(m, 1H, CH), 1.48–1.44(m, 2H, CH₂); MS (ESI) : m/z > 859; Anal. calcd. for C₄₂H₆₂N₁₀O₄: C, 65.97; H, 8.56; N, 17.48; found: C, 65.85; H, 8.48; N, 17.42%.

2.3 Decoration of imine-linked receptors on ZnO nanoparticles

The ZnO nanoparticles were synthesized by mixing the alcoholic solution of Zn(NO₃)₂·6H₂O (595 mg, 2.0 mmol) with alcoholic solution of NaOH (120 mg, 3.0 mmol). A white product was separated out and the product was washed with ethanol and dried at 150°C.

The polymer compound **3** (804 mg, 3 mmol) was taken along with ZnO nanoparticles (100 mg) in dry CHCl₃ and solution was refluxed for 15 h. The progress of the reaction was monitored with IR and UV–vis absorption spectroscopy by taking a small sample from the reaction mixture. Upon completion of reaction, a light yellow coloured solid product was separated by filtration. The product was washed with chloroform and dried under vacuum. Hence, the formation of polymer dye **3**-decorated ZnO nanoparticles were characterized with DLS, SEM and XRD analyses. Figure 2 shows the proper decoration of imine-linked receptors (polymer dye **3**) on ZnO nanoparticles.

2.4 Synthesis of polymer–ruthenium-based composite dye

The polymer compounds (604 mg, 3 mmol) were taken along with RuCl₃ (100 mg) in dry MeOH (20 ml) and the solution was refluxed for 8 h. The progress of the reaction was monitored with IR and UV–vis absorption spectroscopy by taking a small sample from the reaction mixture. Upon completion of reaction, the solution was concentrated,

cooled and stirred with petroleum ether. A pale yellow coloured solid product was separated by filtration. The resultant product was washed with dichloromethane and dried in vacuum over anhydrous calcium chloride. Polymer Schiff base showed strong absorption band in the region of 1665 cm^{−1}. However, upon complexation with the metal it shifted to lower frequency, indicating the formation of the metal complex with CH=N. The formed polymer–ruthenium composite dye was used as a good light sensitizer (photon absorber) in the fabrication of ZnO-based DSSCs. In this research work, we have chosen ruthenium chloride (RuCl₃) as a sensitizer instead of N719 or black dye. N719 as a sensitizer material has pronounced remarkable applications in the field of DSSCs. In fact, we are impressed with the use of this dye, which encouraged us to investigate the structured features of N719 dye. It was found that the material consists of **Ru** as metal centre and guarded by the ligation sides of sp² nitrogen provided by bi-pyridyl moiety (Scheme 1).

Hence under our studies, we have provided the sp² nitrogen from imine linkages of our polymer and parallel to N719, we have used **Ru** as metal centre. Synthetically N719 is tedious to prepare, while with our present system it can be prepared by a simple condensation reaction and moreover in quantitative yield.

2.5 Fabrication of ZnO-based DSSCs

A DSSC is mainly composed of two electrodes, including a transparent conducting metal oxide material generally made of ITO or FTO glass. The photoanode is made up of a wide bandgap semiconductor materials, such as ZnO, TiO₂, CdSe or SnO₂ [30]. The solar cell is assembled with the insertion of a thin layer of ZnO nanoparticles capped by polymer dye molecules (acted as a photoanode) on one side of an ITO conductive glass, a ruthenium dye (acted as photosensitizer), a liquid electrolyte and a counter-electrode (another ITO conductive glass coated by carbon from candle flames). The layer of wide bandgap semiconductor ZnO nanoparticles

Figure 2. Decoration of polymer dye **3** (imine-linked receptors) on ZnO nanoparticles.

Scheme 1. Ru metal ions with nitrogen from imine-linked receptors.

absorbs UV light and sensitized with the polymer dye molecules, which sense/absorb maximum photon energy in the visible range of light (400–700 nm) spectrum. The current assembly of ZnO-based DSSCs allows electronic conduction between two electrodes of the cell. The photo excitation of the polymer dye from the ground state (V) to the excited state (V^*) leads to the injection of charge carriers in the conduction band of ZnO. The effective surface area of DSSC assembly enhances the light harvesting capacity and minimizes the optical absorption, as layer of ZnO nanoparticles contains excess of free electrons.

The polymer–ruthenium based composite dye was used as a light harvester with the main sample, i.e., sample A in the final assembly of ZnO-based DSSCs. The nanocrystalline powder of ZnO was mixed in an aqueous medium with organic additive (acting as binder) homogeneously. The polymer dye **3** molecules were continuously adsorbed on the surface of ZnO nanoparticles. The layer of final dye-capped ZnO nanoparticles was pasted on a cleaned and dried ITO conductive glass sheet acted as a photoanode. This dye-capped ZnO sheet (surface area, $A = 1 \text{ cm}^2$) was air-dried at room temperature (25°C) for 30 min. The conductive side of carbon dust (obtained from candle flame) coated counter electrode was placed on top of the anode sheet. A liquid electrolyte (iodide/triiodide (I^-/I_3^-)) based solution was placed from the top of one of the conductive edge of the cell. The I^-/I_3^- based liquid electrolyte penetrates into imine-linked ZnO nanoparticles. I^- and I_3^- continuously reduce the positive-charged dye molecules and I_3^- redox system diffuses the dye ions to cathode. This liquid electrolyte was put into the space between the two conductive electrodes with capillary action. Thereafter, two good black binder clips were used to hold the electrodes of the cell together.

Finally, the circuit assembly of ZnO-based DSSCs for measuring short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor and incident photoelectric

conversion efficiency was ready for working operation. The ZnO photoanode was assembled with the counter-electrode of the DSSCs. The photovoltaic characteristics of ZnO-based DSSCs were measured in the form of photovoltage and current density. For measuring current and voltage curves, a digital multimeter (Omega DMM 101) was connected to the DSSC electrodes (ZnO photoanode and carbon counter electrode) with a set of variable resistances. The xenon light source was selected as an illumination source. The intensity of light source was 100 mW cm^{-2} . This was equivalent to one sun or AM (air mass) 1.5 of photons power that was delivered to the effective surface area (1 cm^2) of ZnO-based DSSCs. The voltage and current characteristics of DSSCs were measured by two important parameters (V_{oc}) and (J_{sc}) from the following relationship:

$$(\eta\%)_{\text{DSSC}} = \text{Current density } (J_{\text{sc}}) \times \text{open-circuit voltage } (V_{\text{oc}}) \times \text{fill factor}/P_{\text{in}}. \quad (1)$$

In equation (1), P_{in} is the input solar power incident onto the DSSCs. When a bias voltage of zero volts (0V) appeared, short-circuit current density (J_{sc}) was measured and when the value of current dropped to 0 amperes, V_{oc} (open-circuit voltage) was measured. The maximum power generated by ZnO-based DSSCs was obtained by the product of V_{max} and I_{max} .

$$\text{Hence, } P_{\text{max}} = V_{\text{max}} \times I_{\text{max}}. \quad (2)$$

Herein, the current I_{max} may be replaced by J_{max} (mA cm^{-2}) for comparing the different photovoltaic values of ZnO-based DSSCs. The performance of DSSCs also belongs to a significant parameter, i.e., fill factor (FF) described in equation (1). FF is the ratio of maximum power to the product of short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) values. So, FF is given as follows:

$$\text{FF} = \text{Maximum power } (P_{\text{max}})/V_{\text{oc}} \times J_{\text{sc}} = V_{\text{max}} \times J_{\text{max}}/V_{\text{oc}} \times J_{\text{sc}}. \quad (3)$$

Fill factor is a typical value of a DSSC and varies between 0 and 1. FF actually describes the shape of photovoltaic curve for DSSCs. Another important parameter is the incident photon to current conversion efficiency (IPCE). This is a very important factor of the DSSCs, which measures the total percentage of the absorbed light or photons getting converted into electric current by DSSCs under AM 1.5 sun illuminations. IPCE may be defined as follows:

$$\text{IPCE} = 1240[J_{\text{sc}}(\text{mA cm}^{-2})]/[\lambda(\text{nm}) \cdot P_{\text{in}}(\text{mW cm}^{-2})]. \quad (4)$$

Hence, the overall performance of ZnO-based DSSCs is basically dependent on the characteristics of factors mentioned above. For obtaining better performances (efficiency) from DSSCs, lot of research efforts had been carried throughout the world to implement, evaluate and analyse the various solar cell fabrication methods, the stability of dyes used, thickness of photoanode layer, performance of liquid

electrolyte and conductive electrodes, the effect of processing factors on the synthesized materials [24–26].

3. Results and discussions

This section describes the morphology and structural investigations of imine-linked receptors decorated ZnO nanoparticles in terms of determining their size and shape.

3.1 SEM analysis

The morphology of imine-linked receptors decorated ZnO nanoparticles were examined by SEM (JEOL JSM-6610) operated at 15 kV. SEM image of imine-linked receptors decorated ZnO nanoparticles appears to be homogenous, distinct and non-aggregated, as shown in figure 3a. The SEM micrograph shows an average grain size of ZnO in the range of 66 nm. The imine-linked receptors bound across whole of the surface of ZnO nanoparticles. Hence, the agglomeration of ZnO surface was highly reduced after decoration with imine-linked receptors. The energy dispersive spectra image of imine-linked receptors decorated ZnO nanoparticles confirmed the presence of finely dispersed zinc, carbon, oxygen in the nanoparticles, shown in figure 3b.

The proper decoration of imine-linked receptors to ZnO nanoparticles (as shown in figure 2) indicates a complete formation of conductor (photoanode) used in the fabrication of DSSCs. The performance of ZnO-based DSSCs typically depends on two main factors: (i) molecule structure of dye used and (ii) morphology and aggregation of dye molecules. Besides of these parameters, anchoring group of polymer dye **3**, an electrolyte material with redox couple and addition of polymer–ruthenium composite photosensitizer also play an important role in the most favourable working of ZnO-based DSSCs under simulated sun illuminations. The photosensitizer design is basically a donor–acceptor substituted π -conjugated link. The acceptor part of capped dye molecules attached to ZnO nanoparticles. The attached functional group with the ZnO surface is a carboxaldehyde anchoring group.

During the binding formation, the binding groups of polymer dye (imine-linked receptors) interact with surface aldehyde groups attached to the ZnO nanoparticles. The performance of the attached anchoring group to ZnO nanoparticles was observed from its absorption in the visible and near-infrared regions of the solar spectrum.

3.2 Structural investigation (XRD and DLS spectra)

Crystallite size of the synthesized imine-linked receptors decorated ZnO nanoparticles were characterized and analysed by XRD technique for the purpose of comparison. We have synthesized uncapped ZnO nanoparticles using the appropriate precursors. By using Debye-Scherrer's equation [23], particle size of uncapped ZnO nanoparticles was found to be 42 nm. Figure 4 shows the XRD spectra of the imine-linked receptors decorated ZnO nanoparticles, which again confirms the formation of the stable wurtzite structure of ZnO nanoparticles. Size of imine-linked receptors decorated ZnO nanoparticles was computed and calculated using the Debye-Scherrer formula: $D = 0.9\lambda/(\beta \cos \theta)$, where D is the diameter of the crystallite nanoparticle, β the full-width at half maxima and λ the value of the wavelength of the copper (Cu) radiation. The sample of imine-linked receptors decorated ZnO nanoparticles was oriented along a plane, which appears at $2\theta = 31.92^\circ, 32.96^\circ, 33.59^\circ, 34.38^\circ, 36.97^\circ, 38.14^\circ, 40.24^\circ, 43.57^\circ, 47.91^\circ$ and 53.82° , respectively. This is different than non-decorated ZnO nanoparticles with the d-spacing values compared to the standard JCPDS card (36-1451). The comparison confirms the formation of stable wurtzite structure of the imine-linked receptors decorated ZnO nanoparticles. The broadening of the XRD peaks at different plane values confirms the smaller size of the imine-linked receptors decorated ZnO nanoparticles in comparison to the size of undecorated ZnO nanoparticles.

The particle size of imine-linked receptors decorated ZnO nanoparticles was found to be in the range of 28.34 nm using Debye-Scherrer equation. The XRD spectra of imine-linked ZnO nanoparticles confirmed the absence of impurities and

Figure 3. SEM image of ZnO nanoparticles: (a) magnified image and (b) energy dispersive spectra of imine-linked receptors decorated ZnO nanoparticles.

Figure 4. XRD spectra of imine-linked receptors decorated ZnO nanoparticles.

Figure 5. DLS spectra of imine-link decorated ZnO nanoparticles.

high purity of imine-linked ZnO nanoparticles. The imine linked receptors decorated ZnO nanoparticles confirmed the stability with the hexagonal wurtzite shape. DLS image analysis, as shown in figure 5, depicts the size of imine-linked receptors decorated ZnO nanoparticles in the range of 23.57 nm. Comparatively, the particle size of ZnO nanoparticles measured by XRD and SEM analyses were found to be different. In the XRD spectra measurements, the size of imine-linked receptors decorated ZnO nanoparticles was found to be less than the size of ZnO nanoparticles measured with SEM.

3.3 Analysis of fluorescence spectra

The fluorescent spectra of samples A and B of ZnO nanoparticles decorated by imine-linked receptors (polymer dye **3**) and polymer–ruthenium composite dye as a light sensitizer have been recorded at an excitation wavelength of 325 nm using the Xenon source at room temperature conditions. The fluorescence spectra of ZnO samples labelled A and B, as shown in figure 6, exhibited strong and narrow high peaks in the ultraviolet region followed by a widened spectrum

Figure 6. Fluorescence spectra of samples A (polymer dye **3** + ZnO) and B (polymer–ruthenium composite dye + ZnO).

peaks in the visible region of light. The fluorescence spectra of samples A and B exhibited enhanced (narrow peaks) excitations at 350 and 354 nm, respectively. The presence of the peak at 354 nm corresponds to the exciton emission/UV emission in ZnO nanoparticles. Samples A and B showed different peaks at 453 and 462 nm in the visible region, respectively.

Before addition of ruthenium chloride as a sensitizer in sample A, the fluorescence response of imine-linked receptors decorated ZnO nanoparticles appends at 453 nm in the visible region of light spectrum. This peak corresponds to blue band of the spectrum. After addition of ruthenium–polymer composite dye (acted as a photosensitizer) to ZnO nanoparticles in sample B, the fluorescence response becomes more interesting. The fluorescence intensity shows a peak at 462 nm in the visible region of solar spectrum. The fluorescence results confirmed more coupling of UV emission with imine-linked decorated ZnO nanoparticles, which enabled the device to be used for transparent solar cell/display applications [31,32]. The imine-linked receptors

decorated ZnO nanoparticles showed strong visible emission, which was due to high S/V ratio of ZnO nanoparticles. Further, significant peaks had been observed in the IR emission region at 692 and 703 nm for samples A and B. The fluorescence spectra of samples show blue-green emission for broadened peaks formed from surface defects present in the ZnO material.

3.4 UV-Visible absorption analysis

The optical absorption spectra of ZnO samples labelled as A and B (with polymer dye **3** or imine-linked receptors, and polymer-ruthenium composite dye as a sensitizer) are shown in figure 7. The absorption spectra of samples A and B reflect the difference in light harvesting capability for optimal photovoltaic performance of ZnO-based DSSCs. The UV-vis absorption spectra were recorded at room temperature. Significant absorbance peaks were recorded at 380, 404, 448 and 453 nm. The imine-linked receptors decorated ZnO nanoparticles in sample A showed the absorbance peak at 380 and 448 nm. The polymer-ruthenium composite dye

as light absorber in sample B showed more electron transfer from valence band to conduction band within the ZnO nanoparticles.

Sample A (polymer dye **3**-capped ZnO nanoparticles) showed low absorbance peak at 380 nm, in figure 7, while sample B showed high absorbance peak with polymer-ruthenium composite dye acting as a good light harvester. The absorbance band around 404 to 453 nm (for sample B) was due to $\pi - \pi^*$ transition for imine-linked receptors decorated ZnO nanoparticles. This corresponds to a charge transfer between the donor and acceptor sections of polymer dye **3** molecules after capping of 2-FC with PEI. The shifts in the absorbance spectra from 380 to 453 nm for samples A and B was due to the quantum confinement effect among the individual ZnO nanoparticles [33].

3.5 Photovoltaic performances of ZnO-based DSSCs

The current density and photovoltage characteristics of imine-linked receptors decorated ZnO-based DSSCs have been recorded for samples A and B under (AM 1.5G) simulated solar illuminations. We have compared the photovoltaic performance of imine-linked receptors decorated ZnO DSSCs (sample A) with polymer-ruthenium composite dye-based ZnO DSSCs (sample B), as shown in figure 8. The various solar cell parameters, e.g., current density, open-circuit voltage, FF and solar energy to electricity conversion efficiency (η) of ZnO-based DSSCs were recorded and calculated, the results are presented in table 1. The polymer dye **3**-based ZnO DSSCs (sample A) showed significant values of the short-circuit current density ($J_{sc} = 5.30 \text{ mA cm}^{-2}$) and open-circuit voltage ($V_{oc} = 0.67 \text{ V}$). The corresponding values of its maximum current density and voltage are $J_{max} = 5.04 \text{ mA cm}^{-2}$ and $V_{max} = 0.49 \text{ V}$, respectively. The value of FF for imine-linked receptors decorated ZnO-based DSSCs was calculated as 0.695. The solar energy to electric conversion efficiency (η) was calculated from equation (i). The η for sample A-based ZnO DSSCs was calculated as 2.469%.

Figure 7. UV-Vis spectra of samples A (polymer dye **3** + ZnO) and B (polymer-ruthenium composite dye + ZnO).

Figure 8. Current density and photovoltage performances for different DSSCs: samples A (polymer dye **3** + ZnO-based DSSCs) and B (polymer-ruthenium composite dye + ZnO-based DSSCs).

Table 1. Current–voltage characteristics of samples A and B based ZnO dye-sensitized solar cells under AM 1.5 simulated solar illuminations.

Name of sample	Open-circuit voltage, V_{oc} (V)	Short-circuit current density, J_{sc} (mA cm ⁻²)	Fill factor	Efficiency of DSSCs ($\eta\%$)
(A) Polymer dye 3 + ZnO	0.67	5.30	0.695	2.47
(B) Polymer–ruthenium composite dye + ZnO	0.72	8.14	0.654	3.83

Table 2. Comparison of N719 and RuCl₃ photosensitizers for ZnO-based DSSCs.

Structure	Photosensitizer	Efficiency (η)
ZnO NP	N719	0.44% (ref. [34])
ZnO NP	N719	2.10% (ref. [35])
ZnO NP	N719	2.22% (ref. [36])
ZnO NP	N719	2.02% (ref. [37])
ZnO NP	Polymer dye 3 (imine-linked receptors)	2.47% (present result)
ZnO NP	Polymer dye 3 + RuCl ₃	3.83% (present result)

After addition of ruthenium chloride to imine-linked receptors (polymer dye **3**) decorated ZnO nanoparticles, the light harvesting performance of DSSCs increased interestingly. The sample B-based DSSCs has shown higher values of the short-circuit current density ($J_{sc} = 8.14$ mA cm⁻²) and open-circuit voltage ($V_{oc} = 0.72$ V) than sample A-based DSSCs. The corresponding values of its maximum current density and voltage recorded were $J_{max} = 7.823$ mA cm⁻² and $V_{max} = 0.49$ V, respectively.

The calculated value of FF for sample B was 0.654. Similarly, the solar energy to electric conversion efficiency (η) was calculated as stated above in equation (i). The η for sample B-based ZnO DSSCs was calculated as 3.832%. After comparing with N719 sensitizer-based ZnO DSSCs [34–37], our present results revealed that the addition of polymer–ruthenium composite dye enhanced the light harvesting tunnel to the effective surface area of the solar cell.

As shown in table 2, the addition of RuCl₃ sensitizer with the initial sample of imine-linked receptors decorated ZnO nanoparticles (sample A) increases the overall power conversion efficiency of the DSSCs. Comparatively, it has been analysed that the polymer–ruthenium metal complex acted as composite dye is better than the N719 sensitizer used in the DSSCs.

Hence, the overall power conversion efficiency of sample B-based ZnO DSSCs increased by 1.36% compared to the polymer dye **3**-based ZnO DSSCs (sample A). This increment in the solar power to electric energy conversion efficiency was due to binding of imine-linked receptors and ruthenium dye molecules to ZnO nanoparticles, which prevented the aggregation among ZnO nanoparticles [31].

4. Conclusions

In the proposed research work, we had synthesized, characterized and evaluated the optoelectronic and photovoltaic performances of imine-linked receptors decorated ZnO-based DSSCs. For evaluating the photovoltaic performances of DSSCs, we used a dying agent 2-FC with PEI. The formation of the imine-linked receptors (polymer dye **3**) had been decorated to ZnO nanoparticles during the fabrication of DSSCs. The polymer dye **3**-decorated ZnO nanoparticles and polymer–ruthenium composite dye-based ZnO DSSCs had shown good optical properties and excellent photovoltaic performances. The polymer–ruthenium metal complex dye-based ZnO DSSCs had shown a highest power conversion efficiency of 3.83%, which was enhanced by 1.36% of polymer dye **3**-based ZnO DSSCs. In this research work, we had also observed that the proper linkage of imine group receptors and ruthenium dye molecules to ZnO nanoparticles lead to good light harvesting capability of the solar cell. The proposed research work can also be implemented in the fabrication of various optoelectronic applications other than solar cells, such as in light-emitting diodes, night vision sensors and molecular television displays.

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