Efficiency of Solar Cells Employing Natural Dyes with Plasmonic Nano Particle Based Photo Anode

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To cite this article:
Kirti Sahu, Mahesh Dhonde, Khushboo Purohit, V. V. S. Murty. Efficiency of Solar Cells Employing Natural Dyes with Plasmonic Nano Particle Based Photo Anode. Journal of Photonic Materials and Technology. Vol. 3, No. 1, 2017, pp. 1-5. doi: 10.11648/j.jmpt.20170301.11

Received: September 27, 2016; Accepted: October 12, 2016; Published: March 17, 2017

Abstract: Cheap and efficient dye sensitized solar cells (DSSCs) can be prepared using natural dyes responding in visible region of solar spectrum. Localized surface Plasmon resonance (LSPR) plays a very important role for the improvement in the efficiency of DSSCs by using Plasmonic nanoparticles (PNPs) for exploiting the visible portion of the solar radiation by transferring the energy from dye to PNP. This energy transfer from dye to low cost semiconductor TiO₂ through PNP increases the overall photo catalytic activity. In the present study, natural and synthetic dyes are prepared and the optical transmittance and absorbance of the dyes are measured in the wavelength range of 250nm to 850nm using UV-Vis spectroscopy and they are used in DSSC. Natural dyes extracted from fruits and synthetic dye based on Ru metal complex is used as sensitizers. Photo Conversion Efficiency (PCE) of the solar cells utilizing different dyes are compared. Out of the various natural dyes, beetroot and strawberry extracts based dyes show good absorbance in the visible range of electromagnetic spectrum. On the other hand synthetic dye based on Ru complex shows strong absorbance over a wide range of visible spectrum. The absorbance increases with increase in concentration of Ru in ethanol. The extracts of beetroot, strawberry and mixed fruits show a peak in absorbance spectra at 501nm, 416nm and 332nm respectively, indicating the absorption over wide range of visible spectrum. Maximum efficiency of solar cell obtained with synthetic and natural dyes are 5% and 1.5% respectively.

Keywords: Plasmonic Nano Particles, Transmittance, Absorbance, DSSC, Synthetic Dyes, Natural Dyes

1. Introduction

Dye sensitized solar cell (DSSC) was inspired by the energy and electron transfer mechanisms in natural photosynthesis. Natural dyes based solar cell is a low cost and eco-friendly concept to enhance efficiency of DSSC. DSSCs with PNPs are more efficient as compared to pure TiO₂ based DSSCs [1, 2], due to their ability to scatter light back into the photovoltaic structure. Metal Nano Particles (NPs) are placed on top of the solar cell or incorporated inside the photoactive layer of the solar cell. The radiative decay of the LSP modes into propagating electromagnetic waves is observed as a scattering of incident light by the NPs. The scattering properties of large NPs (with diameter > 40 nm) have often been used to increase the optical path length within solar cells and consequently to enhance the short-circuit photocurrent density.

When used with environmental friendly components for the energy generation, DSSCs are proven to be the best alternative energy source. But TiO₂ based DSSC is not very efficient due to its large band gap corresponding to the absorption of sunlight limited to ultra violet region of solar spectrum. On the other hand solar cells based on Si possess low band gap hence Si based solar cells are more efficient due to their absorption of sunlight in both UV and visible region. Except the semiconductors like TiO₂ or Si, the efficiency/performance of solar cell depends on many components used in DSSC. One of the key materials to be considered in DSSCs is the sensitizer with suitable structural and physical properties capable of absorbing sunlight over a wide range of wavelengths. Both natural and synthetic sensitizers (dyes) have the property to absorb sunlight in a very wide region of solar spectrum. By choosing suitable dye, the incident photon to current efficiency (IPCE) of the TiO₂ based DSSC can be improved in visible range.
Out of various synthetic dyes, Ruthenium complex dyes are capable of sensitizing DSSCs with high conversion efficiencies [6]. However, Ru based complexes are very costly and hazardous to environment. Natural dyes are the alternate solution for the suitable sensitizer because its pigments are easily and safely extracted from plants and environmental friendly [8] with low cost, hence they are considered as one of the suitable option for dye sensitized solar cells in future research [10]. Natural dyes based DSSCs have low efficiency and demands parametric variation to increase the performance of the DSSC. The low cost DSSCs with high performance can be designed by using natural dyes.

The main limitations of using semiconductor photo catalysts, such as TiO$_2$ and iron (III) oxide (Fe$_2$O$_3$), for large scale applications have been the short range light response, poor light absorption rate, and high recombination rate of photo generated carriers, which result in low solar energy conversion efficiencies. By using suitable dye and metal Plasmonic nanoparticles (PNPs) onto conventional semiconductor photo catalysts e.g., TiO$_2$, cadmium sulfide (CdS), and Fe$_2$O$_3$, the incident photon to current conversion efficiency (IPCE) can be improved [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28].

2. Mechanism of Dye Sensitized Solar Cells Based on PNP$_s$

DSSC consists of two transparent conducting electrodes coated with pure TiO$_2$ or metal doped TiO$_2$ nanoparticles known as photo electrode and carbon or platinum coated electrode act as counter electrode, dye (sensitizer) which absorbs sunlight over a wide range of solar spectrum and electrolyte (redox couple) which regenerates dye and maintain continuity in the circuit.

The PNP$_s$ efficiently absorb visible light through localized surface Plasmon resonance (LSPR) and convert it into holes and electrons in the nearby semiconductors. Upon light irradiation, the electric field will displace the conduction electrons relative to the nuclei, inducing a large electric dipole. Simultaneously, a restoring force arises because of the Coulomb attraction between electrons and nuclei, which results in resonant oscillation of the conduction electrons at a certain frequency. This LSPR generally occurs when the PNP$_s$ are considerably smaller than the wavelength of the incident light. By increasing absorption cross section as compared to physical cross section, the LSPR of PNP$_s$ can lead to very efficient absorption of light which can enhance efficiency of DSSCs up to several times. LSPR induces electric dipoles which oscillate with the frequency of the incident photon which ultimately increases the intensity of the incident electric field [11, 29].

The mechanism of DSSC with different energy levels is shown in the figure. 1. Photons with different wavelengths incident on the photo anode of the cell and penetrate into the dye layer since both photo anode and the pure or doped TiO2 nano crystals are transparent to visible light. If the energy of the incident photon is close to the energy gap of the dye molecule, gets absorbed by the dye and promoting one electron from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of the dye [30, 31]. The excited electron will then be injected into the conduction band of TiO$_2$ through the interfacial bonds between the dye and the TiO$_2$, and collected by the counter electrode. The hole which was generated by photon excitation remains on the molecule during the process since the HOMO of dye is separated from all other energy levels. The hole eventually will be filled up by electrons from electrolyte ions. At the same time, reduction of oxidized dye by iodide produces tri-iodide. The tri-iodide diffuses to a counter electrode and accepts electrons from external load, regenerating the iodides. The overall process will provide electron flow from the working electrode to the outer circuit [32, 33]. The dye would be regenerated by the electrolyte solution and would get ready for the next photon [33].

3. Materials and Methods of Dye Preparation

3.1. Preparation of Natural and Synthetic Dye as Sensitizer

For natural dyes preparation, juice of various fruits have been extracted and mixed in a suitable amount of water for obtaining required concentration of the dyes. These freshly prepared extracts have been kept for 24 hours at room temperature and finally filtered for removing unwanted solid residue. Similarly synthetic dyes are prepared from the Ru based metal complex which is in the powder form (Solaronix, Switzerland) and mixed in the ethanol and filtered after keeping the dye over night at room temperature. These dyes are used as sensitizer for the adsorption onto the TiO$_2$ nano particles and plasmonic metal nanoparticles. For keeping the dye solutions stable and usable for a long time, it is kept at low temperature and protected from direct exposure of light.
3.2. Preparation of Dye Sensitized Solar Cells

For making photo anode of DSSCs, TCO with 1cm×1cm dimensions are cleaned by ultrasonicator and dried. Pure TiO$_2$ and Al doped TiO$_2$ paste with nanoparticles size ranging from 12 to 30nm is coated on these TCO by using the doctor blade technique [34]. These coated TCO were sintered at 450°C for 30 minutes and then allowed to cool at room temperature. After cooling, the electrodes are immersed in the different dye solutions for a time period of 24 hours. These electrodes after adsorption of dye molecules on the layer of nanoparticles were rinsed thoroughly to remove the extra dye molecules. The dye adsorbed photo anode and carbon coated counter electrode were assembled in a sandwich type cell and then sealed using a thermoplastic sealing film made of Surlyn (Solaronix, Switzerland). The iodide/ triiodide electrolyte is injected in this sandwich assembly by using the hole provided at the counter electrode and sealed after injection.

4. Results and Discussion

4.1. UV-Vis Spectroscopy

Ruthenium based dyes with different molar concentrations are prepared using ethanol as a solvent at room temperature. The samples are analyzed by using Perkin Elmer Lambda 950. This synthetic dye based on ruthenium complex with different concentrations has strong absorbance in the wavelength range of 450nm to 700nm giving possibility for enhanced efficiency of DSSCs.

The absorbance of the different concentration of the samples based on synthetic dyes and natural dyes is shown in the figure 2 and figure 3 respectively.

Similarly, UV-Vis spectra of natural dyes have shown absorption towards the wavelength range of 330nm to 600nm.

It is observed that the strawberry and beetroot have absorbance peaks at 416nm and 500nm with 3.7 and 3.8A.U. respectively. These results show that the natural dye is an alternate efficient candidate for photovoltaic performance of DSSCs at low cost. Extracts of beetroot and strawberry of extracts show absorption towards visible spectrum. These dyes are prepared by mixing fruit extracts in suitable amount of deionized water with constant stirring for 30 minutes. Even natural dyes have absorption towards higher wavelength range, the efficiency obtained with beetroot and strawberry is not suitable at large scale production because these dyes are not very stable. But the results are quite hopeful and by improving the experimental parameters, the efficiency of natural dyes based DSSC can be enhanced.

The photo response of both natural and synthetic dyes in the visible region for their absorbance is measured by UV-Visible spectrometric technique. Results show that in the visible region of solar spectrum, all the natural dye samples exhibit poor absorbance, except the sample of beetroot and strawberry. While Ru complex based synthetic dyes, exhibiting strong absorbance over the wide range in the visible spectrum. Ru based dye is characterized by large absorption coefficient in the visible part of solar spectrum as well as possess strong stability, efficient electron injection and suitable adsorption properties. The spectrum of the some of the natural dye has shown similar characteristics as Ru dye but at different absorbance range.

4.2. Current Voltage (I-V) Characterization

Photovoltaic performance of the DSSCs is determined using current voltage (I-V) curves. Current voltage characterization of the cell using synthetic and natural dyes is performed under one sun condition with AM 1.5 and maximum input power 100mW/cm$^2$ as shown in the figure 4.
Figure 4. Current voltage response of cell with ruthenium based synthetic and fruits based natural dyes.

Table 1. Record efficiencies of Ruthenium N719 based synthetic and natural dyes based solar cells.

| Sample          | Voc (Volts) | Isc (mA/cm²) | Vmp (Volts) | Imp (mA/cm²) | Fill factor | Efficiency(η) % |
|-----------------|-------------|--------------|-------------|--------------|-------------|-----------------|
| Ru (0.5mM) %    | 0.72        | 11.5         | 0.54        | 9.4          | 0.63        | 5               |
| Ru (0.3mM) %    | 0.69        | 11.1         | 0.59        | 8.13         | 0.60        | 4               |
| Ru (0.1mM) %    | 0.67        | 10.2         | 0.47        | 7.54         | 0.40        | 3               |
| Beetroot %      | 0.69        | 5.4          | 0.43        | 3.7          | 0.45        | 1.5             |
| Strawberry      | 0.69        | 5.09         | 0.42        | 3.1          | 0.43        | 1.3             |
| Mixed dye       | 0.56        | 4.29         | 0.37        | 2.9          | 0.41        | 1               |
| Pomegranate     | 0.66        | 3.17         | 0.34        | 2.3          | 0.37        | 0.7             |
| Black grapes    | 0.50        | 1.74         | 0.26        | 1.16         | 0.25        | 0.3             |

The results are significant in case of synthetic dye and dyes based on fruit extract of beetroot and strawberry.

5. Conclusion

Results obtained from UV-Vis and I-V characterization of synthetic and low cost natural dyes based DSSCs show a comparison as well as great possibility of using DSSCs with natural dyes in a suitable manner. Absorption spectra of beetroot and strawberry, show peaks at 416 nm and 500 nm which are lying in visible range of solar spectrum. I-V characterization is performed under one sun condition and maximum efficiency of 5% and 1.5 % are obtained for the DSSCs based on synthetic and natural dyes respectively. By improving experimental conditions, an efficient and low cost natural dye based DSSC can be designed.

Acknowledgement

Authors are greatly thankful to, K.N. Chaturvedi Govt. Holkar Science College, Indore for providing the laboratory facilities. The authors are also thankful to V. Ganeshan, Mukul Gupta, Vinay Deshpande and Shilpa Tripathi UGC-DAE- Consortium for Scientific Research for their support in characterization of the samples and useful discussions.

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