EFFICIENCY IMPROVEMENT THROUGH IRON COMPLEXATION OF NATURAL DYE RUTIN IN DYE-SENSITIZED SOLAR CELL

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Abstract: Natural dyes are cost effective substitute of costly synthetic and metal dyes used in Dye-sensitized solar cells (DSSCs). In this study DSSCs based on natural dye rutin and its iron complex have been fabricated using quasi-solid state polymeric electrolyte and characterized in terms of photovoltaic properties. Nano crystalline TiO_2 was synthesized in the lab and analysed through Raman spectroscopy. The UV-VIS absorption spectra of TiO_2 thin film before and after sensitization with rutin and its iron complex were recorded. The UV-VIS absorption spectra of dyes solution were also recorded for the same range of wavelength. Increased absorption was observed for rutin iron complex as compared to pure rutin in both forms. Different photovoltaic parameters i.e. short circuit current density, open circuit voltage, fill factor and power conversion efficiency were obtained using J-V curve of these devices. The power conversion efficiencies of rutin and Fe-rutin based devices are found to be 0.21% and 0.41% respectively. Around 95% increment in power conversion efficiency was observed after iron complexation of rutin.

Keywords: rutin, iron complex, quasi-solid polymeric electrolyte, efficiency.

I. INTRODUCTION

Dye sensitized solar cell, also known as Grätzel cell, is an innovative solar cell of third generation [1]. The DSSC was conceptualized by O'Regan and Grätzel in 1991 [2]. DSSC does not require sophisticated facilities and can be fabricated at ambient temperature and remain unaffected by environmental impurity [3].

Basically two types of photosensitizes or dyes are used in DSSCs; organic and inorganic [4]. Organic dyes can be synthetic or natural whereas inorganic dyes are mainly based on metal complex. Though the efficiency of DSSCs based on natural dyes are very low as compared to that of inorganic or synthetic dyes [5], still natural dyes are being investigated as photo sensitizers in the DSSCs because of its low cost, easy availability in natural resources such as flowers, fruits, leaves, bark etc.

In this study natural dye rutin and its iron complex have been used as sensitizer. Rutin is bioflavonoid or plant pigment found naturally in buckwheat, citrus fruits such as lemon, grapefruit, orange, green and black tea etc. Its name was originated from Ruta graveolens, a plant which contains rutin. The role of wide band gap semiconductor TiO_2 and dye is a significant feature for the performance of the DSSC [6].

T. Ma et al. reported 1.12 % efficiency of DSSC based on rutin extract [7], whereas Özacar et al. reported efficiency improvement of DSSC by iron complexation of natural dye quercetin [8]. These DSSCs were based on liquid electrolytes which lack the long term stability. Therefore quasi solid polymeric electrolyte has been used here for the fabrication of DSSCs which improves the stability of devices [9].

II. EXPERIMENTAL DETAILS

2.1 MATERIALS AND REAGENTS USED

Titanium tetra-n butyl oxide, rutin dye, iron (III) chloride ($FeCl_3.9H_2O$), H_2PtCl_6, fluorine doped tin oxide-coated glass substrate (FTO) etc.

2.2 SYNTHESIS OF TiO_2 NANO PARTICLES

TiO_2 nano powder was synthesized using technique reported by Li et al. [10]. Titanium tetra-n butyl oxide (TTB) was used as precursor in this method. 17 ml TTB was mixed with 40 ml of anhydrous ethanol under stirring at room temperature (blend-A). Then 20 ml glacial acetic acid and 40 ml of anhydrous ethanol were blended with 15 ml distilled water (blend-B). Finally blend-A was added drop wise to blend-B and left for vigorous stirring up to 3 hours. After drying at room temperature, the material was crushed. Then the crushed powder was kept at 450 °C for 4 hours. In final step, fine white TiO_2 powder was obtained after crushing.

2.3 FABRICATION OF WORKING ELECTRODE AND SENSITIZATION WITH DYE

Initially screen printable TiO_2 paste was prepared. For this 2 gm of TiO_2 powder was mixed with 10 ml n-butanol in one beaker and 2 gm of TiO_2 powder was mixed with 10 ml deionised water in another beaker. In third beaker 1 gm of ethyl cellulose was mixed with 10 ml n-butanol. All three blends were stirred overnight. Then all three were mixed together and again kept for stirring for 6 hours. Then turpenol and polyethylene glycol were mixed in appropriate amount and homogenised screen printable TiO_2 paste was obtained after continuous stirring for 5 hours.

To prepare working electrode (photo anode), fluorine doped tin oxide-coated (FTO) conducting glass having sheet resistivity of 10-12 Ω/sq was used as substrate after cleaning. For cleaning, the FTO substrate was sonicated using ultrasonic bath (Model: Sonicor SG-3042) with soap solution, acetone and IPA respectively. Then the FTO substrate was cleaned using Plasma cleaner (Model: Harrick Plasma, PDC-002). Thereafter a smooth thin film was prepared by coating the TiO_2 paste on cleaned FTO substrate using screen printing technique. For smooth bonding between TiO_2 and FTO, this photo anode was sintered at 450 °C for two hours.

For sensitization, two different solutions of pure rutin and Fe-rutin complex were prepared. First solution was prepared in methanol having 20 mM concentration of pure rutin. To prepare Fe-rutin complex, 20 mM rutin and 20 mM iron (III) chloride ($FeCl_3.9H_2O$) were mixed in methanol and kept for stirring for one hour in ambient conditions. Both rutin and Fe-rutin solutions were covered with aluminium foil to protect from the light in surrounding. Then prepared working electrodes were immersed in these two solutions separately and left overnight for sensitization process. Finally the working electrodes were washed with the same solvent (methanol) to remove the excess dye.

2.4 PREPARATION OF COUNTER ELECTRODE, ELECTROLYTE AND PACKING OF CELL

The Pt layer coated FTO conducting substrate was used as counter electrode. For this FTO was cleaned by the same method as mentioned earlier. H_2PtCl_6 was mixed in methanol in 1: 10 ratio. This blend was coated on cleaned FTO substrate kept over water bath. Finally this substrate was sintered at 450 °C to be used as counter electrode. Quasi solid polymeric electrolyte was prepared by using method reported by

Chen et al. [11]. A blend of organic solvent n-methyl pyrrolidone (NMP) and gamma butyrolactone (GBL) was taken in 3:7 volume ratios and kept under stirring. The stirring was continued for 24 hours after addition of I_2 (0.1 mM) and KI (0.5 mM) to prepare electrolytic solution protecting from direct light exposure. Finally to get quasi-solid state polymeric electrolyte (SPE) thin film, polyvinyl butyral (PVB) film was immersed into this solution. In the last step, the prepared working and counter electrodes clamped together sandwiching the SPE thin film to fabricate the dye sensitized solar cell.

2.5 MEASUREMENT AND CHARACTERIZATION

The UV-VIS spectra of the pure rutin and its iron complex solutions were recorded. Similarly UV-VIS spectra were recorded for bare TiO_2 thin film on FTO and photo anode sensitized in pure rutin and Fe-rutin in the wavelength range 200 nm-800 nm using UV-VIS spectrophotometer (Model: Specord S 600-analytic jena).

Raman spectra of TiO_2 powder was recorded using Raman Instrument (Model: Avlon Instruments, Raman Station R3) using green laser (532nm) at power 50mW in the frequency range 200-4000 cm^{-1}.

The photovoltaic characterization of fabricated devices having active area of 1 cm^2 was performed using semiconductor parameter analyzer (Model: HP 4145B) under solar light with the input power 61 mW/cm^2. Different photovoltaic parameters short circuit current density (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) were obtained using J-V curves of fabricated DSSCs.

III. RESULTS AND DISCUSSION

3.1 OPTICAL CHARACTERISATION

The UV-VIS absorption spectra of pure rutin and its iron complex in methanol solvent are shown in figure 1. It is clear that there is an appreciable enhancement in absorption over entire range of wavelength i.e. 200 nm to 800 nm.

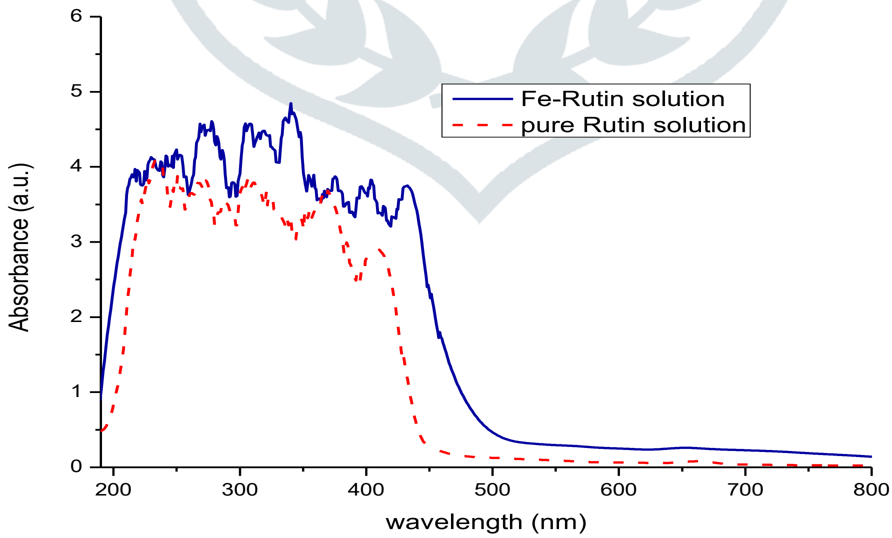

figure 1. UV-VIS absorption spectra of pure rutin and Fe-rutin

This is encouraging outcome which suggests that iron complex of rutin has increased the absorption of photons in the visible region resulting in better efficiency. The UV-VIS absorption spectra of working electrode sensitized in pure rutin and its iron complex is shown in figure 2. It is explicit that the absorption increases significantly for pure rutin and Fe-rutin as compared to that bare photo anode. The improvement in absorption after iron complexation is also very significant. This increment in absorption improves the efficiency. Such considerable absorption improvement suggests that iron complexation of rutin has increased dye loading resulting in improved photo current.

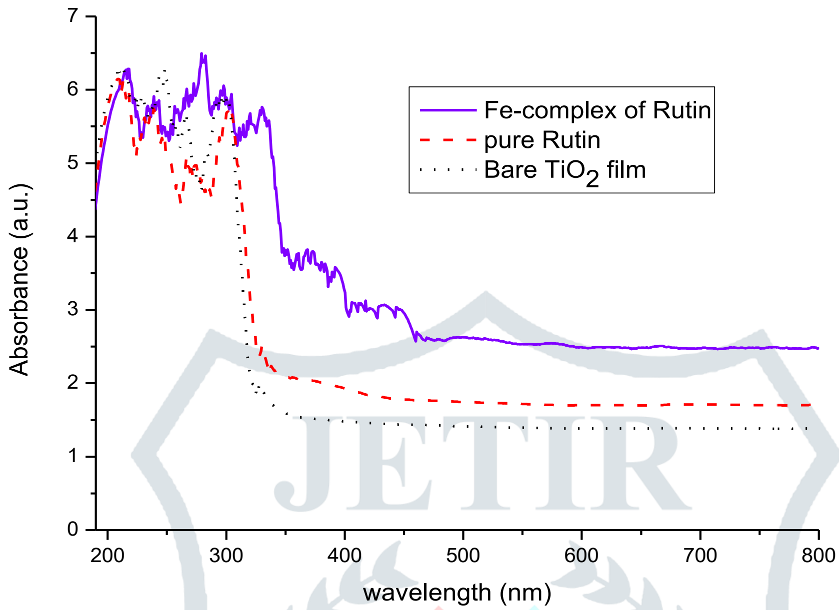

figure 2. UV-VIS absorption spectra of sensitized and bare photo anode

3.2 STRUCTURAL ANALYSIS THROUGH RAMAN SPECTROSCOPY

The Raman spectra of thin film of TiO_2 on FTO and the synthesized TiO_2 powder are shown in figure 3. It is explicit that three characteristics peaks of tetragonal anatase phase of TiO_2 are present at three strong bands at 400 (B_{1g}), 520 (B_{1g}) and 642 (E_g) cm^{-1}. There is an extra peak observed at 1092 cm^{-1} in the spectrum of thin film which can be attributed to the interface bonding between TiO_2 and FTO.

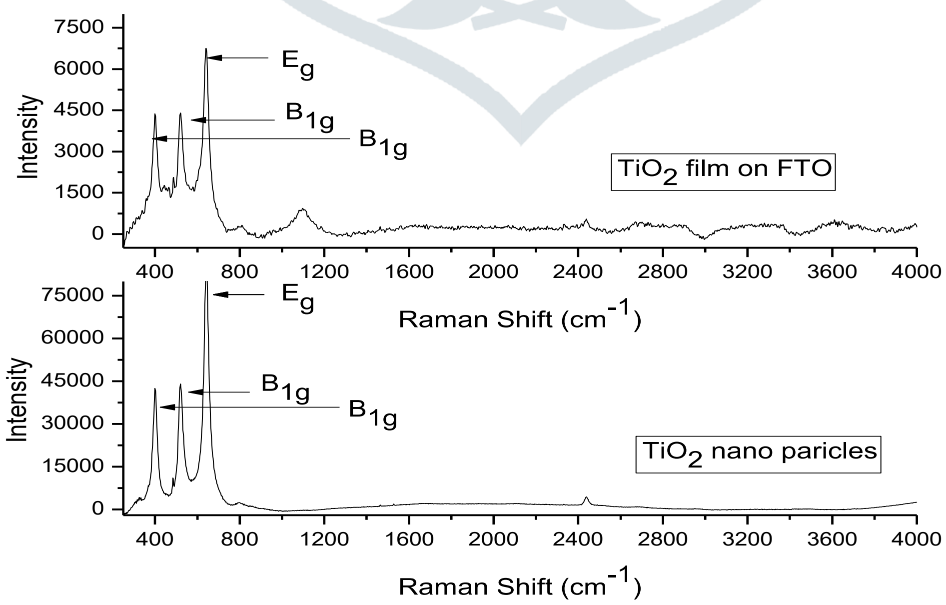

figure 3. Raman spectra of synthesised TiO_2 thin film on FTO and TiO_2 nanoparticles

Hence Raman analysis indicates the formation of anatase phase of TiO_2 nano particles. The anatase phase makes electron transport more feasible as compared to rutile phase giving rise to improved photovoltaic performance [12].

3.3 PHOTOVOLTAIC PROPERTIES

The current-voltage characteristics of the fabricated DSSCs are shown in figure 4. It is quite clear that iron complexation has amplified the amount of dye loading due to which the value of short-circuit density J_{sc} has increased. The value of open circuit voltage V_{oc} is also increased which can be attributed to the better injection efficiency after iron complexation. These facts suggest that iron complexation induces greater dye loading and photon harvesting ability than the pure rutin dye.

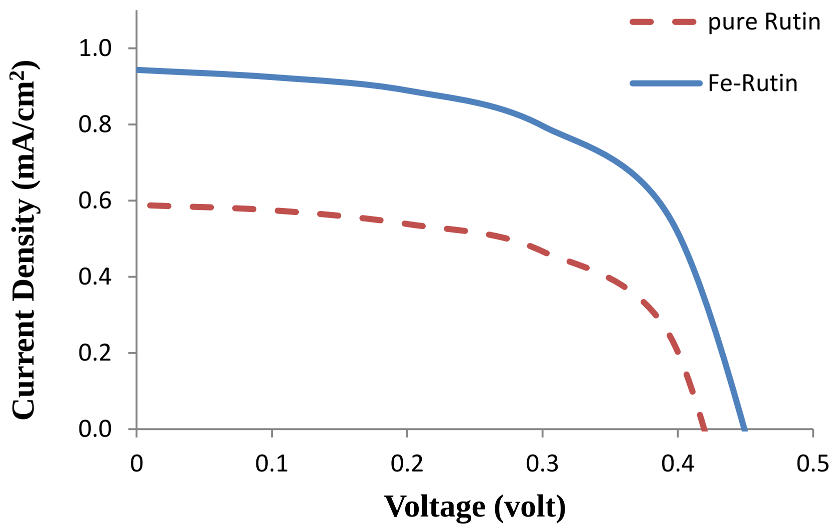

figure 4. current density vs. voltage curves of fabricated DSSCs

It is clear from Table-1 that iron complexation of rutin has imparted a significant improvement in all photovoltaic parameters (V_{oc}, J_{sc}, FF and η). The improved fill factor indicates the better quality of the cell after iron complexation. Slight enhancements are seen in open circuit voltage and fill factor, whereas major change is observed in short circuit current density after iron complexation. The values of short circuit current density for pure rutin and Fe-rutin devices are 0.589 mA/cm^2 and 0.943 mA/cm^2 respectively.

Table-1 photovoltaic parameters of the fabricated DSSC

Device Configuration	V_{oc} (volt)	J_{sc} (mA/cm^2)	Fill Factor (FF)	Efficiency η (%)
FTO/TiO_2/pure rutin/electrolyte/Pt/FTO	0.42	0.589	0.52	0.21
FTO/TiO_2/Fe-rutin/electrolyte/Pt/FTO	0.45	0.943	0.56	0.41

The power conversion efficiencies of rutin and Fe-rutin based devices are found to be 0.21% and 0.41%, respectively. Due to iron complexation, the power conversion efficiency for Fe-rutin device is found to be almost double of the pure rutin device. By restricting recombination, iron complexation has increased both short circuit current density and open circuit voltage. Thus enhanced photo current gives rise to improved power conversion efficiency for Fe-rutin DSSC.

IV. CONCLUSION

The dye sensitized solar cells based on natural dye rutin and its iron complex using quasi solid polymeric electrolyte were fabricated and characterised in terms of optical and electrical properties. The anatase phase of synthesized nc-TiO_2 was confirmed by Raman spectroscopy. The power conversion efficiencies of rutin and its iron complex based devices were found to be 0.21% and 0.41% respectively. The overall increment in power conversion efficiency after iron complexation is around 95%.

Hence these observations suggest that iron complexation of rutin improves the efficiency by enhancing the amount of dye loading and restricting recombination. The utilization of quasi solid polymeric electrolyte is also justified as it helps in improving stability of solar cell; a necessary aspect for the commercial potential.

V. REFERENCES

[1] E. Stathatos, J. of Eng. Sci. & Tech. Rev., 2012, 5, 9-13.

[2] B. O'regan and M. Gratzel, Nature, 1991, 353,737-739.

[3] J. Gong, K. Sumathy, Q. Qiao and Z. Zhou, Renew. & Sust. Ene. Rev., 2017, 68, 234-246.

[4] R. S. Shelke, S.B. Thombre and S.R. Patrikar, Int. J. of Renew. Ene. Reso., 2013,3,54.

[5] M. R. Narayan, Renew. & Sust. Ene. Rev., 2012, 16, 208-215.

[6] S.Shalini, R.Balasundara, S. Prasanna, T. K. Mallick and S. Senthilarasu Narayan, Renew. & Sust. Ene. Rev., 2015, 51, 1306-1325.

[7] H. Zhou, L. Wu, Y. Gao, T. Ma, J. of Photochem. & Photobio. A: Chem.istry, 2011, 219, 188–194.

[8] S. Çakar and M. Özacar, J. Photochem. Photobiol. A Chem., 2017, 346, 512.

[9] N. Prasad, M. Kumar, K.R. Patel and M. S. Roy, AIP Conference Proceedings, 2018, doi: 10.1063/1.5032741.

[10] Y. Li, G. Ma, S. Peng, G. Lu, and S. Li, Appl. Surf. Sci., 2008, 254, 6831-6836.

[11] K.F. Chen, C. H. Liu, H. K. Huang, C. H. Tsai, and F. R. Chen, Int. J. Electrochem. Sci., 2013, 8, 3524-3539..

[12] N. G. Park, J. Lagemaat and A.J. Frank, J. Phys. Chem. B, 2000, 104, 8989.