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Fabrication and comparison of dye-sensitized solar cells by using TiO_2 and ZnO as photo electrode

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ABSTRACT

Five natural dyes were extracted from the peels of *Malus domestica*, *Punica granatum*, *Phoenix dactylifera*, Raphanus *sativus* and *Solanum melongena* by maceration in methanol for application in dye-sensitized solar cells. Their photophysical, electrochemical and photovoltaic properties were investigated. Thin layers of nano materials ZnO and TiO_2 were deposited on FTO glasses by doctor's blade technique. These films were dipped in the dye solution bath for twenty-four hours. The results verified that *Solanum melongena* dye has better efficiency 1.10% as compared to other dyes. We also investigated that TiO_2 is a better photoelectrode as compared to ZnO. By using *Solanum melongena* andTiO_2 nanoparticles we found 1.10% efficiency and 0.67% by using ZnO as photoelectrode. The results indicate that TiO_2 is a better photoelectrode as compare to ZnO. Lower efficiency of the natural dyes as compared to synthetic dyes may be due to lower active contents for DSSCs.

1. Introduction

Dye sensitized solar cells (DSSCs) is a device which converts light energy into electricity by using wide band gap nanomaterials [1]. Dye sensitized solar cells was discovered by Gratzel and his co-worker in 1991 that's why it is also called Gratzel cell. DSSCs got more attention because of their low cost, easy fabrication and good efficiency [2,3]. By using ruthenium and metal free organic dyes 10–12% efficiencies have been achieved and further work is still in progress [4–6]. DSSCs performance depends on metal oxides such as TiO_2or ZnO because dyes anchor with it and transfer electron into semiconductor band gap edge [7].

Initially metal based complex dyes (Ruthenium) and organic dyes were used as working electrode and they have normal to good conversion efficiencies. However, ruthenium dyes contain precious metal that needs tedious synthesis and purification methods, it is also very expensive and it is toxic and can cause eye problems [8,9]. Platinum(Pt) is another metal used to form counter electrode of DSSCs but this metal makes DSSCs expensive so instead of using Pt other kind of materials such as graphene or carbon can be used [10].

Hence, it is possible to use natural dyes and pigments as alternative photo sensitizers with appreciable photophysical and electrochemical properties. Furthermore, natural dyes are environment friendly, very cheap, easily extractable and abundantly available all over the world. Fruit, vegetables and flowers have different shades of colors containing donor as well as acceptor units which can

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be extracted at ambient conditions and can be used in DSSCs [11]. Natural dyes contain chlorophyll, betanins, carotenes, anthocyanins and tannins have successfully been applied in DSSCs [12]. Keeping in view the current work was designed and photosensitizers were extracted from five natural resources and their photophysical and photovoaltaic studies were carried out.

2. Experimental

2.1. Extraction of natural dyes

Three Fruits *Malus domestica* (Apple), *Punica granatum*(Pomegranate), *Phoenix dactylifera*(Date) and two vegetables *Raphanus sativus* (Red Radish) and *Solanum melongena* (Eggplant) were purchased from the local market. The peels were separated from the flesh and seeds. The peels were first washed and dried at room temperature for 15 days under shade. 10 g of each sample was immersed in 90 ml methanol at room temperature in dark for 48 h with occasional shaking. Natural dyes were obtained after filtration.

2.2. Preparation of electrolyte for cyclic voltammeter

Redox potential of the natural dyes was measured by cyclic voltammetry using three electrode system. Platinum was used as working electrode Ag/AgCl wires were used as the reference electrode at scan rat of 50 mV/s. The electrolyte solution was prepared by 0.1 M tetrabuty lammonium perchlorate ($TBAClO_4$) in distilled water and all three electrodes were immersed in this solution for electrochemical properties.

2.3. Preparation of DSSCs

In order to prepare working electrode for solar cells, FTO (Fluorine-doped tin oxide) glass was washed with deionized water, acetone, ethanol and isopropanol in ultrasonic bath to remove impurities from the glasses [13]. ZnO nanoparticles were prepared by sol-gel method and TiO_2 nanoparticles were purchased from the market for comparative study. ZnO paste was prepared by Ethanol based solution. First of all, 2 ml solution was prepared by mixing 70% ethanol and 30% distilled water. Then 0.6 g of ZnO nanoparticles were measured by microbalance. The paste was made by mixing ZnO with ethanol based solution. The mixture was sonicated for 15 min to get homogeneous paste. The paste was coated on FTO substrate by doctor blade method. The coated substrate was annealed at 400℃ for 30 min.

TiO_2 paste was prepared by mixing 4 ml deionized water, 0.8 ml acetyl acetone, 0.1 ml triton and 2 g of TiO_2 powder then grinding the mixture for 15 min. The mixture was sonicated for 15 min for getting homogeneous paste The paste was coated on FTO substrate by doctor blade method after that the coated substrate was annealed at 400^0Cfor 30 min. After cooling thin films were immersed in dyes solution for 24 h. Counter electrodes were prepared by using graphite. To evaluate the photovoltaic performance, working electrodes were assembled into a sandwiched type together with graphite counter electrode.

3. Results and discussion

3.1. Photophysical properties

The photophysical properties of five natural dyes were studied by UV–vis spectrophotometer. The UV-VIS absorption of *Malus domestica* (Apple), *Punica granatum* (Pomegranate), *Raphanus sativus* (Red Radish), *Solanum melongena* (Eggplant) and *Phoenix dactylifera* (Date) in methanol were taken and absorption is shown in Fig. 1. Flowers, fruits, vegetables and leaves have different colors in nature and they all contain some pigments that can be used to fabricate dye sensitized solar cells. Anthocyanin is the main molecule which is present in all plant based natural dyes which provides them dark colors. Fig. 1 and Table 1 shows the absorption of extracted dyes. UV–vis analysis has shown that *Solanum melongena* has maximum absorption at 419 nm and *Punica granatum* at 409 nm which

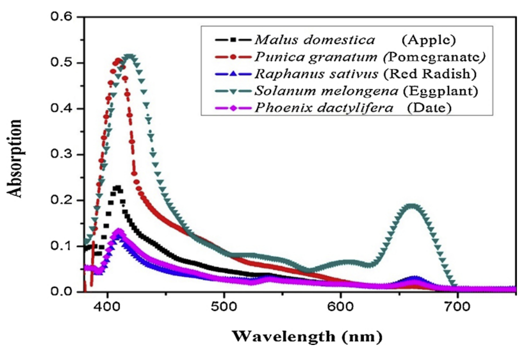

Fig. 1. Absorption Spectra of extracted dyes.

Table 1
Absorption range of extracted dyes.

Dyes (Peels)	π – π* Band	ICT band
Malus domestica(Apple)	408 nm (0.23)	661 nm (0.03)
Punica granatum(Pomegranate)	409 nm (0.50)	663 nm (0.013)
Raphanus sativus (Red Radish)	408 nm (0.13)	661 nm (0.029)
Solanum melongena (Eggplant)	419 nm (0.52)	660 nm (0.19)
Phoenix dactylifera (Date)	409 nm (0.149)	663 nm (0.022)

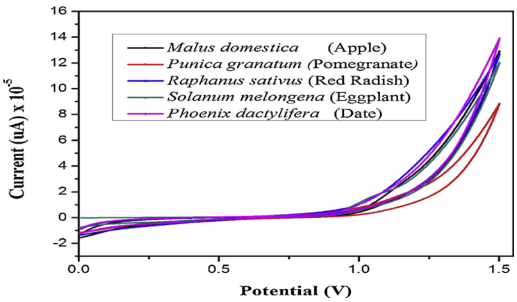

Fig. 2. Cyclic Voltammetry of extracted dyes.

could be recognized to the existence of anthocyanin. Fig. 1 has shown that the λ_{max} for all the five dyes are almost at the same range this is because all kind of fruits and vegetables based dyes have almost same kind of molecules. As shown in Fig. 1, the UV–vis spectra for all five dyes exhibit two bands appearing at 400–450 nm and 600–700 nm respectively. The first band which is at shorter wavelength is ascribed to π-π* transition of electron and Fig. 1 shows that the transition of electron is higher for *Solanum melongena* and *Punica granatum* as compare to other dyes, the absorption for these dyes is at 419 nm and 409 nm respectively. The second band at longer wavelength recognized to the intermolecular charge transfer (ICT) from donor to acceptor [7]. It can be seen in Table 1 that the intermolecular charge transfer is highest for *Solanum melongena* at 661 nm which indicated that the efficiency by using this dye will be higher.

From UV–vis spectra it can be concluded that the transition of electron and ICT is highest for *Solanum melongena* dye and it can also be seen that all extracted dyes are suitable for fabricating dye sensitized solar cells.

3.2. Electrochemical properties

Fig. 2 shows the Cyclic voltammetry (CV) of the extracted dyes. CV is used to investigate the probability of electron transfer of electron from the excited state of the dyes to the conduction band of the semiconducting oxide and redox behavior was also studied by CV. Oxidation potential of the dyes figures out the HOMO level of the dyes and from Fig. 2 we found that all the dyes' molecules have almost same level which is 1.5 eV. They all have same HOMO level because all dyes have almost same molecules.

Oxidation peaks can be clearly seen in all the five dyes which indicate the oxidation behavior of the dyes i.e. it will lose electron on oxidation similarly reduction behavior also can be viewed which indicate that these dyes have regeneration capacity. The small hub on potential 1.0 V for all dyes shows the electron transformation power and dyes and the curve for *Solanum melongena* is higher than other dyes which shows that this dye has more conversion power and its efficiency will be higher than other dyes. From Fig. 2 it can be concluded that current dyes can be used for DSSCs purpose.

3.3. Photovoltaic properties

3.3.1. Photovoltaic performance by using ZnO as photoelectrode

Fig. 3 shows the J–V curves of assembled DSSCs with natural dyes extracted from peels of fruits and vegetables. Table 2 represents all parameters of fabricated dye sensitized solar cells by using ZnO nanoparticles. The DSSC sensitized by *Solanum melongena* have shown the highest efficiency of 0.67% with (J_{sc}3.85mAcm^{-2}, V_{oc} of 0.28 V and a fill factor of 0.62). *Punica granatum* exhibits the second highest efficiency of 0.63 with (J_{sc} 3.68 mAcm^{-2}, V_{oc} 0.29 V and fill factor of 0.59). The third highest efficiency is 0.51% by using natural dye of *Malus domestica* with (J_{sc} 2.44 mAcm^{-2}, V_{oc} 0.28 V and fill factor of 0.75). By using *Phoenix dactylifera* we got 0.45% (J_{sc} 2.45 mAcm^{-2}, V_{oc} 0.29 V and fill factor of 0.63) and by using *Raphanus sativus* we got 0.35% (J_{sc} 2 mAcm^{-2}, V_{oc} 0.28 V

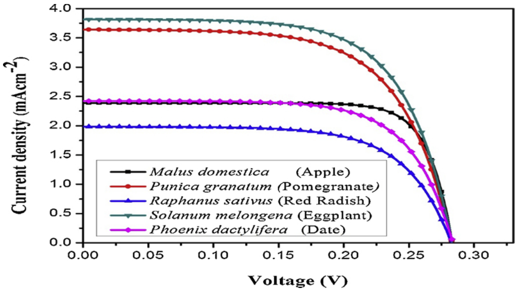

Fig. 3. J–V Curves of DSSCs by using different dyes and ZnO as photoelectrode.

Table 2
Photovoltaic parameters of DSSCs based on natural dyes by using ZnO photoelectrode.

Name (Peels)	*Jsc*(mA/cm^2)	*Voc* (V)	*FF*	η *(%)*
Malus domestica (Apple)	2.44	0.28	0.75	0.51
Punica granatum (Pomegranate)	3.68	0.29	0.59	0.63
Raphanus sativus (Red Radish)	2	0.28	0.63	0.35
Solanum melongena (Eggplant)	3.85	0.28	0.62	0.67
Phoenix dactylifera (Date)	2.45	0.29	0.63	0.45

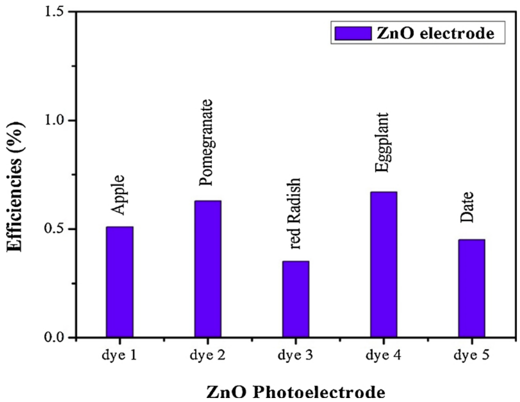

Fig. 4. Comparison of efficiencies by using ZnO electrode.

and fill factor of 0.63). *Solanum melongena* and *Punica granatum* have shown higher efficiencies as compare to other dyes due to the UV–vis absorption range. These two dyes have higher absorption in visible range that is why their light to electricity conversion power is higher than other dyes. Efficiency comparison between extracted dyes using ZnO electrode can be seen in Fig. 4.

3.3.2. Photovoltaic performance by using TiO_2 as photoelectrode

For comparison study we have also used TiO_2 nanoparticles as photoelectrode, sandwich type DSSCs were fabricated with the five natural dyes and their photovoltaic performance was measured. Fig. 5 shows the J–V curves of assembled DSSCs with natural dyes with TiO_2 electrode. Table 3 represents all parameters like; Jsc, Voc and FF of fabricated dye sensitized solar cells. The DSSC sensitized by *Solanum melongena* have shown highest efficiency of 1.10% with (J_{sc}4.51mAcm^{-2}, V_{oc} of 0.33 V and a fill factor of 0.74). *Punica granatum* exhibits the second highest efficiency of 1.008% with (J_{sc} 4.5 mAcm^{-2}, V_{oc} 0.32 V and fill factor of 0.70). The third highest efficiency is 0.85% by using natural dye of *Malus domestica* with (J_{sc} 4.48 mAcm^{-2}, V_{oc} 0.32 V and fill factor of 0.59). By using *Phoenix dactylifera* we got 0.81% (J_{sc} 4.21 mAcm^{-2}, V_{oc} 0.33 V and fill factor of 0.58) and by using *Raphanus sativus* **we** got 0.73% efficiency with (J_{sc} 3.12 mAcm^{-2}, V_{oc} 0.33 V and fill factor of 0.71). Here, we can see that the transformation of electron is higher in TiO_2 electrode than ZnO electrode that's why short current density and open circuit voltage is increased and the power conversion efficiency of DSSCs is also increased. Table 3 have all parameters of the DSSCs by using extracted natural dyes as photosensitizer and TiO2 as photoelectrode. Fig. 6 shows the efficiency comparison between extracted dyes by using TiO_2photoelectrode.

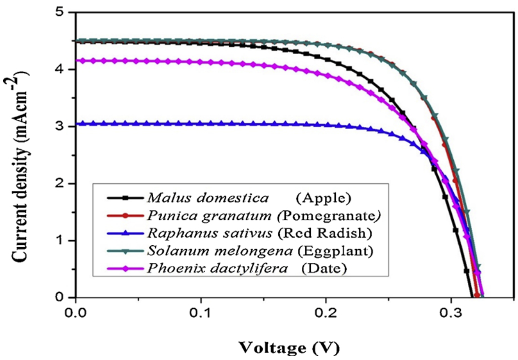

Fig. 5. J–V Curves of DSSCs by using dyes and TiO_2 as photoelectrode.

Table 3
Photovoltaic parameters of DSSCs based on natural dyes by TiO_2photoelectrode.

Name (Peels)	*Jsc* (mA/cm^2)	*Voc* (V)	*FF*	η *(%)*
Malus domestica(Apple)	4.48	0.32	0.59	0.85
Punica granatum(Pomegranate)	4.5	0.32	0.70	1.008
Raphanus sativus(Red Radish)	3.12	0.33	0.71	0.73
Solanum melongena(Eggplant)	4.51	0.33	0.74	1.10
Phoenix dactylifera(Date)	4.21	0.33	0.58	0.81

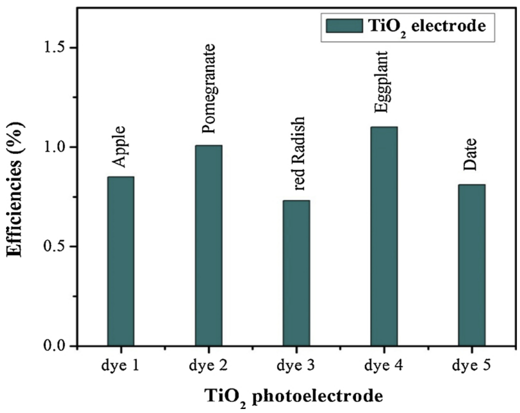

Fig. 6. Comparison of efficiencies by using TiO_2 electrode.

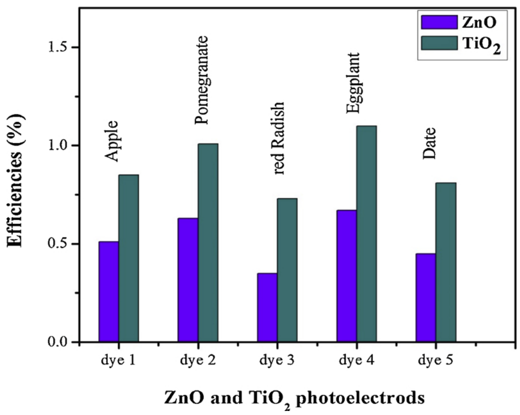

Fig. 7. Comparison of efficiencies.

3.3.3. ZnO VS TiO2 as photoelectrode

In this work, comparison of ZnO and TiO_2 nanoparticles as photoelectrode for dye-sensitized solar cells. Nanoparticles of TiO_2 and ZnO provides large surface area for the adsorption of dye molecules. the excited electrons from the dye molecules are injected into the conduction band of the semiconducting oxide films. That's why semiconducting film is important in DSSCs. By comparing, light to electricity conversion efficiencies of five natural dyes and using both semiconducting oxide films it was found that the TiO_2 is a better photoelectrode than ZnO. The power conversion efficiency is less for ZnO photo anode due to low recombination power and lower transformation of electron from the dye molecules to the conduction band of ZnO [14]. The other reason for low efficiency by ZnO photoelectrode is probably due to insufficient surface area for the adsorption of sensitizer and is that ZnO is not stable as compare to TiO_2 film. The Comparison is shown in Fig. 7.

4. Conclusion

In this reported work, five natural dyes were extracted from the peels of *Malus domestica*, *Punica granatum*, *Phoenix dactylifera*, Raphanus *sativus* and *Solanum melongena* and used as sensitizer for dye sensitized solar cells. Their UV absorption and cyclic voltammetry and photovoltaic studies were carried out and described in detail. UV–vis showed that the absorption is higher for *Solanum melongena* and Punica *granatum* as compared to other samples. A comparison of ZnO and TiO_2 nanoparticles as photoelectrode and five extracted dyes as sensitizers under same conditions was carried out. the result demonstrated that Solanum *melongena's* (Eggplant) dye gives better results as compare to other dyes because its better UV absorption range and higher short circuit current density. It was also concluded that TiO_2 is a better photoelectrode than ZnO as it gave better photovoltaic performance in term of short circuit current density, open circuit voltage and fill factor. For *Solanum melongena* the short current increased from 3.85 mA/cm^2 to 4.51 mA/cm^2 and the open circuit voltage increased from 0.28 V to 0.33 V by using TiO_2 thin film as compared to ZnO thin films.

Furthermore, we found 1.10% efficiency by using TiO_2 and 0.67% by ZnO as photoelectrode and *Solanum melongena* as photosensitizer. It may be due to better anchoring of dye molecule to the TiO2 and better electron injection from the excited state of the dye to the conduction band edge.

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