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Dyes Extracted from Safflower, Medicago Sativa, and *Ros* Marinus Oficinalis as Photosensitizers for Dye-sensitized Solar Cells

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In this work, three extracts of plant leaves were used as sensitizers for dye-sensitized solar cells (DSSCs). These plants are Safflower, Medicago sativa and *Ros* marinus oficinalis. The natural dyes were extracted before and after grinding the plant leaves. The UV-VIS absorption spectra of the three extracts in ethyl alcohol solution were measured. The DSSCs were assembled using TiO_2 films on Fluorine-doped tin oxide (FTO) coated glass. The DSSCs sensitized with the extracts of grinded leaves showed a better performance compared to those sensitized with un-grinded leaves with the highest efficiency of 0.115 % was obtained for the DSSC sensitized with Medicago sativa. The performance of the DSSCs sensitized with Safflower and Ros marinus oficinalis was significantly improved by acid treatment of the FTO substrates. Impedance spectroscopy of the fabricated cells was also carried out.

Keywords: Dye-sensitized solar cells, Plant leaves, Impedance spectroscopy.

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1. INTRODUCTION

Solar energy research is growing rapidly since the evolution of silicon-based solar cell technology in the early 1950s. This tremendous work has led to the first and second generations of solar cells, which are commonly used today. Research is currently growing up into the third generation solar cells which include polymer-based solar cells, nanocrystalline cells, and dye-sensitized solar cells (DSSCs). Since the invention of DSSCs by O'Regan and Grätzel in 1991 [1], they have received a considerable attention because of their low cost, tunability, flexibility, ease of manufacturing and environmental friendship. In DSSCs, a thin film of nano-particles of wide band gap semiconductor, mostly titanium oxide (TiO_2), is deposited on top of conducting glass electrode (FTO). The films are sensitized by natural or synthetic dye for absorption of light. The electrons in the highest occupied molecular orbital (HOMO) in the dye molecules are excited to the lowest unoccupied molecular orbital (LOMO). The excited dye then releases electrons to the close-lying state of TiO_2. Electrons then transport through the load. To complete the circuit, a counter electrode receives the electrons, giving it to an I^-/I_3^- used as a redox couple to replenish electrons to the dye molecules. With TiO_2-based DSSCs, efficiencies of up to 11 % have been obtained using ruthenium polypyridyl complexes as a sensitizer [1]. Recently, an improvement in efficiency (15 %) was reported by Grätzel's group [2]. The efficiency and stability of these cells can be affected by various factors like light absorption by the dye, porosity of the TiO_2 film, surface area of the nano-particles, electron transport and so on. Controlling these parameters can be obtained by various ways such as using different dyes [3-15], semiconductors with different band gaps or morphology [16] or electrolytes [17-19]. Although the performance of natural dyes yields lower efficiency than synthetic dyes, its benefits as low cost, ease of manufacturing, environmentally safeness, and abundance, encouraged researchers to focus on the improvement of its efficiency.

Impedance spectroscopy has been used efficiently to study the electrochemical properties of many photodevices such as DSSCs, because of its sensitivity and ability to separate individual overlapping processes involved in these cells. This leads to a variety of network models suggested by many researchers [20, 21].

The aim of this work is to describe the properties and analyze the working process of porous film electrodes fabricated with TiO_2 nanoparticles, anchored with three natural dyes extracted from plant leaves for DSSC application. These plants are Safflower, Medicago sativa and Ros marinus oficinalis. Using UV-VIS spectrophotometer, the absorption spectra of the extracts of Safflower, Medicago sativa, and Ros marinus oficinalis in ethyl alcohol solution were measured. The natural dyes extracted from the raw materials before and after grinding were used to fabricate DSSCs. By measuring the current-voltage characteristics of the cells, the photovoltaic parameters such as the conversion efficiency were determined. Also the FTO sheets were treated by acidic solutions of HNO_3, H_2SO_4, and H_3PO_4 before spreading the TiO_2 layer by doctor-blade method to study the DSSC performance. The working process of the assembled solar cells was analyzed by studying Nyquist and Bode curves presented by impedance spectroscopy.

2. EXPERIMENT

2.1 Preparation of Natural dye Sensitizers

Three natural dyes were extracted from the leaves of Safflower, Medicago sativa, and Ros marinus oficinalis. The leaves of the plants were washed with dis-

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tilled water and dried at 70 °C. Some leaves of each kind were crushed to form a fine powder using a mortar. The process of dye extraction was carried out before and after grinding the leaves so that two extracts were obtained for each dye: one was obtained before grinding the leaves and the other after grinding. 1 gm from each material (before grinding) was immersed in 5 ml of absolute ethyl alcohol at room temperature in dark for one day. Moreover, 1 gm from each material powder was immersed in 5 ml of absolute ethyl alcohol at room temperature in dark for one day. At last the solutions were filtered to get rid of the remaining solid parts. All natural extracts were kept in a dark place.

2.2 Fabrication of Dye-sensitized Solar Cells

Fluorine-doped tin oxide (FTO; resistance: 12-14 Ω/cm^2; transmittance: 82-84 %; purchased from Xinyan Technology Ltd, Hong Kong) conductive glass sheets were first cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. A TiO_2 paste was prepared by grinding 0.1 g of polyethylene glycol and 0.05 g of TiO_2 nanopowder for half an hour until a smooth fine paste was obtained. The FTO conductive glass sheets were divided into two groups. The samples of one group were immersed in one of three different acidic solutions of HNO_3, H_2SO_4 and H_3PO_4, each of 0.1 M concentration, for 10 min whereas the samples of the other group were not treated by the acids. The TiO_2 paste was deposited on the FTO samples of the two groups by doctor-blade technique in order to obtain a TiO_2 thin layer of 0.25 cm^2 area. The TiO_2 layer was dried at 70 °C for 20 min before sintering at 450 °C for 40 min. After cooling down to 70 °C, the TiO_2 films were soaked in the natural extracts for 24 h in the dark. A Pt-coated FTO was used as a counter electrode which was sandwiched with dyed TiO_2 layer to form the solar cell. Finally a redox (I^-/I^3) electrolyte solution was injected to fill the space between the cell electrodes. In conclusion, we have fabricated three sets of DSSCs. One set was fabricated using untreated FTO and dyed with the extracts obtained before grinding the leaves. The second set was also prepared using untreated FTO but dyed with the extracts obtained after grinding the leaves. The third one was fabricated using the acidic treated FTO and dyed with the extracts of the grinded leaves.

2.3 Characterization and Measurement

Using UV-VIS spectrophotometer (Thermoline Genesys 6) with wavelength range extended from 350-800 nm, the representative UV-VIS absorption spectra for the dye extracts in ethyl alcohol solution were measured. The current density (J)-voltage (V) characteristic curves were carried out under illumination of the fabricated cells with 100 mW/cm^2 irradiations using high pressure mercury arc lamp. The J-V characteristic curves were measured using National Instruments data acquisition card (USB NI 6251) in combination of a Labview program. In the J-V measurements, a voltage, usually in the range between – 1 to 1 volts, is applied to the illuminated solar cell and the resulting current is measured. Impedance spectroscopy was carried out using an SP-200 potentiostat (Biologic, USA), with the frequency ranging from 100 Hz to 200 kHz.

3. RESULTS AND DISCUSSION

3.1 Absorption Spectra of Natural Dyes

The UV-VIS absorption spectra of the extracts of safflower, Medicago sativa, and Ros marinus oficinalis in ethyl alcohol as a solvent are shown in Fig. 1. It is clear from the figure that both safflower and Medicago sativa have clear peaks at 420 nm for safflower and at 490 nm for Medicago sativa. On the other hand, Ros marinus has several peaks but in the measurements range it shows a peak at 415 nm.

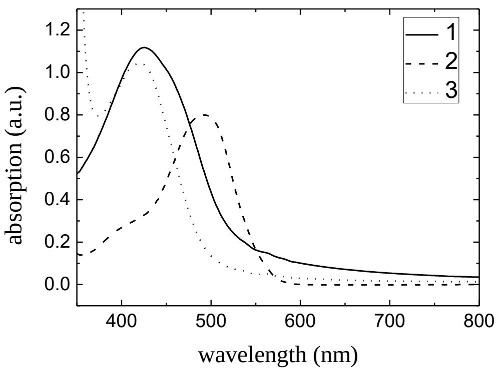

Fig. 1 – The absorption spectra of the extracts of (1) Safflower, (2) Medicago sativa and (3) Ros marinus oficinalis

3.2 Photovoltaic Properties

In this subsection, the J-V characteristic results of the two DSSC sets fabricated using untreated FTO and dyed with the three extracts obtained before and after grinding the leaves are presented. The J-V characteristic curves for the set sensitized with extracts of safflower, Medicago sativa, and Ros marinus before grinding the leaves are shown in Fig. 2 whereas those of the cells sensitized with the three extracts after grinding the leaves are illustrated in Fig. 3. It is noticed that the DSSCs sensitized with the extracts of grinded leaves gave better results than those sensitized with the extracts of ungrinded leaves. This can attributed to the better solubility of all the compounds of the raw material when grinding the leaves. In Table 1, the Photoelectrochemical parameters including short circuit current J_{sc}, open circuit voltage V_{oc}, fill-factor FF, and the conversion efficiency η are presented. The response of the DSSC sensitized with

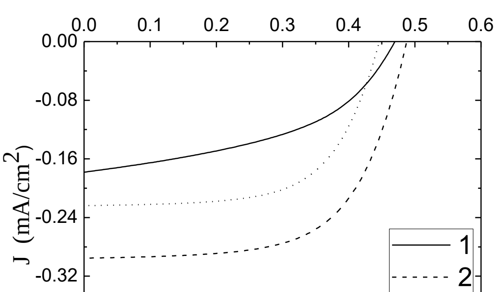

Fig. 2 – Current density–voltage curves for the DSSCs sensitized by (1) Safflower, (2) Medicago sativa, and (3) Ros marinus oficinalis, before grinding the leaves

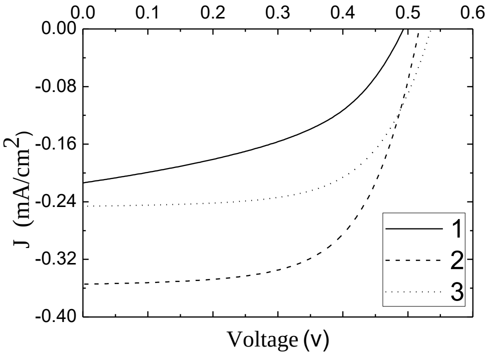

Fig. 3 – Current density-voltage curves for the DSSCs sensitized by (1) Safflower, (2) Medicago sativa, and (3) Ros marinus oficinalis, after grinding

Medicago sativa was the best with $J_{sc} = 0.295$ mA/cm^2, $V_{oc} = 0.488$ V, $FF = 52$ %, and the conversion efficiency $\eta = 0.089$ % before grinding the leaves and $J_{sc} = 0.354$ mA/cm^2, $V_{oc} = 0.516$ V, $FF = 63.1$ %, and $\eta = 0.115$ % after grinding.

3.3 Impedance Spectroscopy Measurements

Electrochemical impedance spectroscopy (EIS) was employed to analyze charge transport kinetics in the cell. Usually in EIS study, the solar cell is perturbed by a small AC voltage signal. In this work, the DSSCs were perturbed by with a signal of amplitude 10 mV with varying frequency (10 mHz-10 MHz). According to the DSSC response, Nyquist and Bode curves were obtained for the DSSCs sensitized by safflower, Medicago sativa, and *Ros* marinus extracts. Nyquist and Bode curves are illustrated in Figs. 4 and 5, respectively. The impedance parameters were calculated from Figs. 4 and 5 and listed in Table 2 in which R_S is the charge recombination resistance, R_{CT} is the charge transfer resistance, and CPE coefficient (α) is the constant phase element due to double layer capacitance (C_{dl}). Also the effective lifetime of electrons τ was estimated. From these results we can conclude that $R_{CT} >> R_S$ for the three DSSCs which indicates fast electron transport and long lifetime of electrons in the film. On the other hand, the values of the CPE coefficient (α) for DSSCs sensitized with safflower, Medicago sativa, and Ros marinus extracts are in the range $0.6 < \alpha < 1$ which means diffusion with deviations and surface roughness in the structure of the double layer capacitor.

3.4 FTO Acidic Treatment

The *J-V* characteristic curves for the DSSCs prepared using acidic treated FTO are shown in Fig. 6. The photoelectrochemical parameters of these cells are listed in Table 3. The *J-V* characteristics were tested under 100 mW/cm^2 intensity. The table also shows the photoelectrochemical parameters of DSSCs prepared on untreated FTO. Compared to the untreated solar cells, the DSSCs sensitized with safflower and *Ros* marinus exhibited better performance in all parameters with treating the FTO by one of the three acids, with a remarkable one for *Ros* marinus. For DSSCs sensitized with *Ros* marinus the J_{sc} increased from 0.246 mA/cm^2 to 0.385 mA/cm^2 when treating FTO by HNO_3 solution, the V_{oc} values improved from 0.534 V to 0.556 V and photoconverging efficiency raised by 244 %. The efficiency enhancement was around 195 % when treating FTO with H_2SO_4 or H_3PO_4. In the case of DSSCs synthesized with safflower, the efficiency improvement was about 147 % when treating the FTO by HNO_3 solution. In this case, the J_{sc} reached 0.284 mA/cm^2 and the V_{oc} was 0.504 V. In general the effect of three acidic solutions can be ranked beginning with the best one as HNO_3, H_2SO_4 then H_3PO_4.

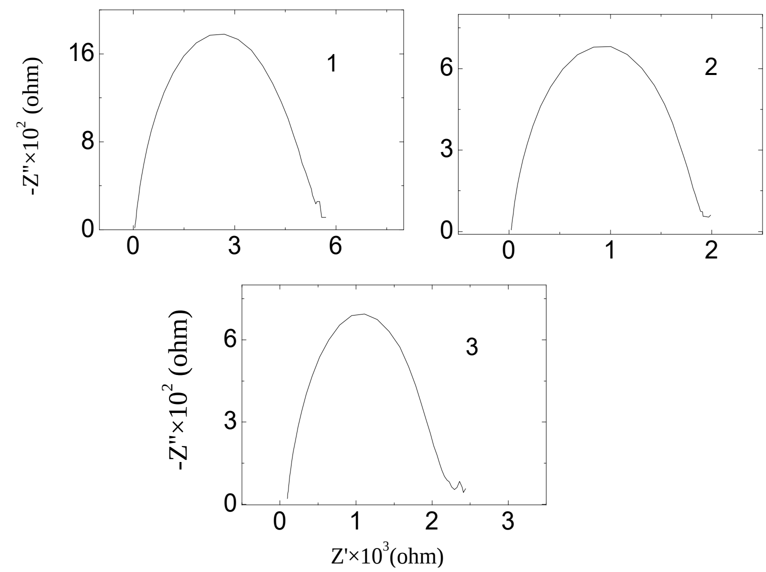

Fig. 4 – EIS Nyquist plots of DSSCs sensitized by (1) safflower, (2) Medicago sativa and (3) *Ros* marinus under an illumination of 100 mW/cm^2 and – 0.7 V applied voltages

Table 1 – Photoelectrochemical parameters of the DSSCs sensitized by three natural dyes extracted with ethyl alcohol as a solvent before and after grinding

Natural dye	J_{sc} (mA/cm²)		V_{oc} (V)		*FF* (%)		η (%)	
	before	after	before	after	before	after	before	after
Safflower	0.177	0.214	0.469	0.492	46.7	46.4	0.0388	0.049
Medicago sativa	0.295	0.354	0.488	0.516	52.5	63.1	0.0890	0.115
Ros marinus oficinalis	0.223	0.246	0.445	0.534	40.1	45.2	0.0398	0.059

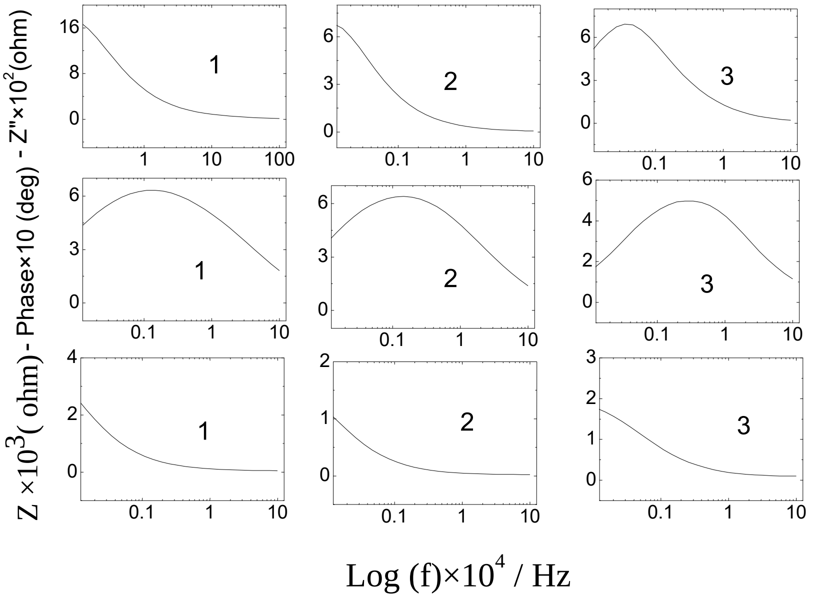

Fig. 5 – Bode plots of DSSCs sensitized by (1) safflower, (2) Medicago sativa, and (3) *Ros* marinus under an illumination of 100 mW/cm² and – 0.7 V applied voltages

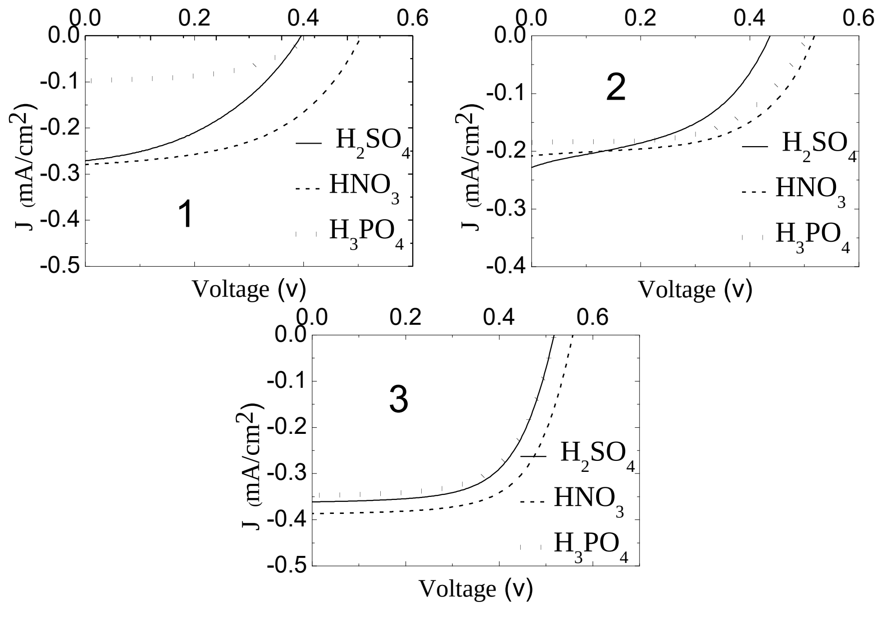

Fig. 6 – Current density–voltage curves for the DSSCs sensitized by (1) Safflower, (2) Medicago sativa, and (3) *Ros* marinus oficinalis, prepared on acidic treated FTO

Table 2 – The impedance spectroscopy parameters of the DSSCs sensitized by the extracts of safflower, Medicago sativa, and *Ros* marinus

Natural dye	R_S (Ω)	R_{CT} (Ω)	C_{dl} (μF)	α (CPE coefficient)	τ (ms)
Safflower	80.5	5702	2.67	0.73	15.26
Medicago sativa	24.4	1974	5.83	0.8	11.55
Ros marinus	101.5	2337	1.20	0.69	2.81

Table 3 – Photoelectrochemical parameters of the untreated and acidic treated FTO DSSCs

Natural dye	Safflower			Medicago sativa			*Ros* marinus		
	J_{sc} (mA/cm^2)	V_{oc} (V)	η (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	η (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	η (%)
untreated	0.214	0.492	0.049	0.354	0.516	0.115	0.246	0.534	0.059
HNO_3	0.284	0.504	0.072	0.256	0.516	0.061	0.385	0.556	0.144
H_2SO_4	0.266	0.396	0.045	0.284	0.438	0.045	0.356	0.517	0.117
H_3PO_4	0.096	0.411	0.022	0.230	0.504	0.054	0.342	0.516	0.114

4. CONCLUSION

In this work, DSSCs were fabricated using TiO_2 as a semiconducting material and synthesized by the plant leaves of Safflower, Medicago sativa and Ros marinus oficinalis. The natural dyes were extracted before and after grinding the plant leaves. It was found that the extracts obtained from grinded leaves yielded higher efficiency than those obtained from un-grinded leaves. Short circuit current density, open circuit voltage and the cell efficiency improved when using the extracts of grinded leaves for all natural dyes. Another efficiency improvement was obtained for the DSSC sensitized with safflower when FTO was treated with HNO_3 whereas a significant efficiency enhancement was obtained for the DSSC sensitized with Ros marinus when FTO was treated with HNO_3, H_2SO_4 or H_3PO_4. For DSSCs sensitized with Ros marinus, the efficiency enhancement was around 195 % when treating FTO with H_2SO_4 or H_3PO_4 whereas it was about 147 % for DSSCs synthesized with safflower, when treating the FTO by HNO_3 solution.

Impedance spectroscopy was carried out and Nyquist and Bode curves were plotted for the DSSCs sensitized by safflower, Medicago sativa, and Ros marinus extracts. The impedance parameters such as charge recombination resistance R_S, charge transfer resistance R_{CT}, and the constant phase element due to double layer capacitance (C_{dl}) were determined. The effective lifetime of electrons was also calculated. It was found that $R_{CT} >> R_S$ for the three cells which indicates fast electron transport and long lifetime of electrons in the film.

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