

Dyes extracted from *Trigonella* seeds as photosensitizers for dye-sensitized solar cells

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Abstract In this paper, the extract of *Trigonella* seeds was used as sensitizer for dye-sensitized solar cells (DSSCs). The natural dye was extracted from the seeds using water and alcohol as solvents for the raw material. The UV–Vis absorption spectra of *Trigonella* extract solution and dye adsorbed on TiO₂ film were measured. DSSCs sensitized by *Trigonella* extracted using water as a solvent exhibited better performance with efficiency of 0.215 %. The performance of the fabricated DSSCs was attempted to enhance by acid treatment of the FTO substrates with HNO₃, H₃PO₄, and H₂SO₄. Electrochemical impedance spectroscopy of the fabricated cells was also carried out.

Keywords Renewable energy · Solar cells · Dye-sensitized solar cells · Natural dyes

Introduction

Nowadays, the world is looking forward for obtaining clean renewable alternative energy source which is essential for developing our current lifestyle and economic growth. This was an inevitable result of the imbalance between the production and consumption of fossil fuel. Solar energy was one of the most promising technologies

that have been extensively studied. The outcome of these studies was construction of three generations of solar cells. The bulk crystalline-silicon solar cell was the first generation which has an acceptable efficiency, but its high cost and industrial requirements led to the second generation known as thin film solar cells. The second generation is cheaper but has low efficiency, so the third generation came to keep the benefits of easy manufacturing and low cost while looking for better converging efficiency. Dye-sensitized solar cells (DSSCs) invented by O'Regan and Grätzel [1] are famous by their simple preparation process accompanied with a reasonable efficiency. The main structure of this kind of solar cells is built of a photoactive electrode consisting of a tin-oxide conducting glass mounted by a nanostructured wide band gap metal-oxide semiconductor thin film anchored to suitable dye molecules, which have the ability to be excited by absorbing light photons. The excited electrons are injected from the dye lowest unoccupied molecular orbital (LUMO) to the semiconductor conduction band, passing through an external load to a platinum counter electrode. To complete the circuit the photoactive and the counter electrodes are sandwiched with the space between them is filled by an iodide–triiodide electrolyte. The main rule of the electrolyte is to regenerate the oxidized dye. Conversely, the electrolyte will be regenerated from the counter electrode. Each component of this simple structure has been extensively discussed by many researchers seeking for efficiency improvement. Many wide band gap semiconductors like (TiO₂, ZnO, SnO₂) were studied with different morphologies (nanopowder, nanotubes, nanowires) [2–4]. Furthermore, the vital rule for the dye in the working mechanism of DSSCs in light harvesting was investigated. Many chemical groups like homoleptic dyes (N3, N719, N749) developed by Grätzel [5, 6] heteroleptic sensitizers (Z907,

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K19, K77), ruthenium polypyridyl complexes, and organic dyes (triphenylamine, carbazole, phenothiazine) have recorded encouraging efficiencies up to 10–12 %. The high cost and environmental harms of these dyes turned the attention toward natural pigments like anthocyanins, chlorophylls, and hypericin [7–9] extracted from plant leaves, roots, flowers, seeds, and fruits [10–16]. In spite of natural dyes low efficiencies compared to ruthenium complexes, they attracted the attention of many researchers working on enhancing their performance by studying the effect of various factors in the extraction process, such as drying, grinding, temperature, anchorage time, and using different compounds of solvents [17, 18]. Natural juglone dye was obtained from the outer shell of walnut fruit by hot extraction method followed by doping using aluminium, copper and iron metals and used as a photosensitizer of DSSCs [19]. Fast production of the ZnO nanorods by bottom up approach using arc discharge method in deionized water was carried out for DSSC applications [20]. The synthesis of copper-doped polyaniline (NPANI-Cu-X) was performed in many solvents [21]. The obtained PANI was employed as counter electrode in a DSSC configuration. DSSC bilayer design was developed using an $\text{Fe}^{2+}/\text{Fe}^{3+}$ (ferrocene) liquid electrolyte and natural dyes extracted from *Hypericum perforatum*, *Rubia tinctorum* L. and *Reseda luteola* [22].

Dye-sensitized solar cells have been prepared using natural dyes such as red cabbage, red perilla, rosella, blue pea, and curcumin [23]. The efficiency of the fabricated DSSCs was improved by selecting a proper sensitizer and modifying the surface of FTO by chemical treatment. The FTO surface was treated by HCl and TiCl_4 . Moreover, different organic solvents were used to enhance the extent of sensitization [23].

In this work, the natural dye extracted from *Trigonella* seeds was studied as a photosensitizer of DSSCs. The absorption spectrum of the extract was determined. The effect of using alcohol and water as solvents of the *Trigonella* seeds in the dye extraction was investigated. Pre-acidic treatment to the conductive glass substrates was conducted to improve the DSSC photovoltaic performance. Impedance spectroscopy study was provided to understand the transport of electron and hole carriers, interfacial charge transfer and recombination.

Experimental

Dye preparation

The clean dry seeds of *Trigonella* plant (1st washed with distilled water and dried at 70 °C) were grinded by a mortar to form a fine powder. 1 g of the fine powder was

immersed in 5 ml ethyl alcohol at room temperature and left in dark for 24 h, and then the solution was filtered to obtain the final extract solution. The same procedure was repeated for the same amount of *Trigonella* fine powder but the solvent was replaced with distilled water. Finally, the obtained extracts were kept in dark cold place.

Photoelectrode preparation

A transparent conducting FTO sheets (resistance 12–14 Ω/cm^2 ; transmittance: 82–84 %; Xinyan Technology Ltd, Hong Kong) with dimensions 1 cm \times 1.5 cm were cleaned using ultrasonic bath filled with detergent solution for 20 min, then rinsed with distilled water and dried.

The FTO conductive glass sheets were divided into four groups. The first group was not treated by acids. The second, third, and fourth groups were immersed for 10 min in acid solutions of HNO_3 , H_2SO_4 and H_3PO_4 , respectively, each of 0.1 M concentration.

0.2 grams of TiO_2 nanopowder (P25) was added to 0.1 g polyethylene glycol and the mixture was grinded for 30 min until a fine paste is obtained.

The TiO_2 paste was spread on all the FTO groups by doctor-blade technique, where a thin film was obtained on an area of 0.25 cm^2 . The sintering process started by drying the sheets at 70 °C for 20 min, raising temperature to 180 °C for 10 min, then 450 °C for 40 min. After cooling down to 70 °C, the TiO_2 thin film samples were soaked in the *Trigonella* natural extract for 24 h in the dark.

Assembling of DSSC

The prepared TiO_2 photoelectrode (anode) and a conductive glass sheet plated with platinum by electrodeposition (cathode) were sandwiched to assemble the DSSC. Finally, the space between the two electrodes was filled with a liquid electrolyte solution (I^-/I_3^-) composed of 2 ml acetonitrile (ACN), 8 ml propylene carbonate (*p*-carbonate), 0.668 g potassium iodide, KI, and 0.0634 g iodine, I_2 . Then, the two electrodes were clipped together to form a solar cell ready for light exposure.

Measurement

The UV–Vis absorption spectra of *Trigonella* dye extracted by water and alcohol were measured using Thermoline Genesys 6 spectrophotometer with wavelength range extending from 350 to 800 nm. The representative UV–Vis absorption spectrum of the anchored *Trigonella* extract on TiO_2 thin film layer was measured by collecting a diffuse reflectance spectrum with a V-670, JASCO spectrophotometer then transforming it into absorption spectrum according to the Kubelka–Munk relationship. Moreover,

the cyclic voltammetry was used for the measurement of the HOMO, LUMO, and energy band gap. The current density–voltage (J – V) characteristic curves of the DSSCs under study were measured using National Instruments data acquisition card (USB NI 6251) in combination of a Labview program. An applied voltage in the range between -1 and 1 V was applied to the illuminated solar cell during current–voltage measurements. The J – V curves were measured at 100 mW/cm² irradiations using high pressure mercury arc lamp. Electrochemical impedance spectroscopy (EIS) was carried out using an SP-200 potentiostat (Biologic, USA), with the frequency ranging from 100 Hz to 200 kHz.

Results and discussion

Absorption spectra

Trigonella extract UV–Vis absorption spectra in both water and alcohol as solvents are shown in Fig. 1. According to the figure, a clear absorption peak was observed at 400 nm in case of alcohol and another peak at 444 nm for water. A diffuse reflectance spectrum was collected for the Trigonella dye adsorbed on TiO₂ film and transformed to the absorption spectrum according to the Kubelka–Munk relationship [24], $F(R) = (1 - R)^2/2R = k/s = Ac/s$ where R is the reflectance, k is the absorption coefficient, s is the scattering coefficient, A is the absorbance and c is the concentration of absorbing species. When c and s remain the same, the spectrum obtained for Kubelka–Munk function can be considered as absorbance. Figure 2 shows the detected absorption peak at 430 nm for the dye adsorbed on TiO₂ which indicates a red shift towards higher wavelength compared to that of the extract in solution.

The cyclic voltammetry was used for the measurement of the HOMO, LUMO, and energy band gap. It was found

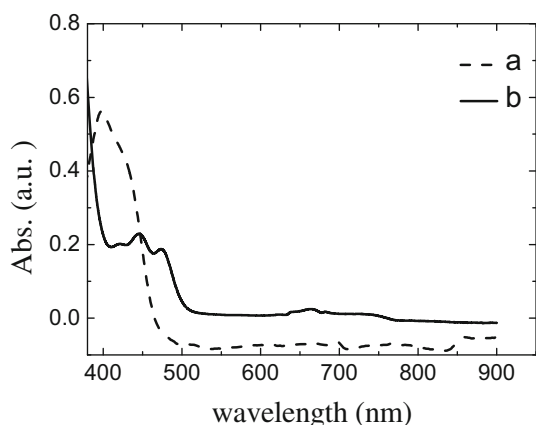


Fig. 1 Light absorption spectra of Trigonella extract dye solution using *a* alcohol and *b* water

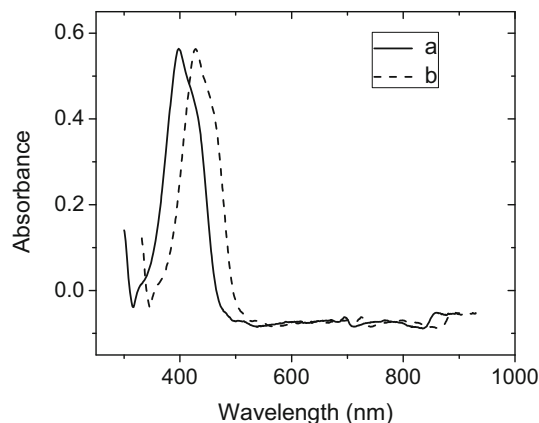


Fig. 2 *a* Light absorption spectra of Trigonella extract dye solution using alcohol and *b* dye adsorbed on TiO₂

that $E_{\text{HOMO}} = 6.28$ eV, $E_{\text{LUMO}} = 3.75$ eV and $E_{\text{opt}} = 2.5$ eV.

Photovoltaic properties

The J – V characteristic curves for DSSCs (fabricated using untreated FTO, 1st group,) sensitized by the natural extract of Trigonella seeds using water and alcohol as solvents are illustrated in Fig. 3. The main photoelectrochemical parameters obtained from Fig. 3 are listed in Table 1. These parameters are short circuit current J_{sc} , open circuit voltage V_{oc} , fill-factor FF, and conversion efficiency η . It is clear from the figure that the performance of DSSCs sensitized by Trigonella extracted using water as a solvent is much better than that of solar cells sensitized by Trigonella extracted with alcohol. Referring to Table 1, $J_{\text{sc}} = 0.371$ mA/cm² with alcohol and $J_{\text{sc}} = 0.747$ mA/cm² with water giving 201 % improvement. On the other hand, $V_{\text{oc}} = 0.599$ V and FF = 48 % with alcohol are almost the same as $V_{\text{oc}} = 0.601$ V and FF = 48 % with

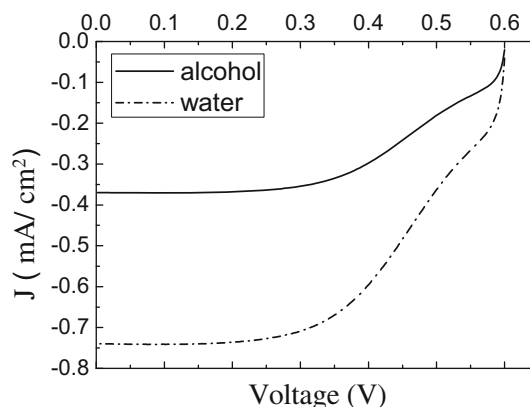


Fig. 3 Current density–voltage curves for the DSSCs sensitized by Trigonella seeds dye using alcohol and water as solvents

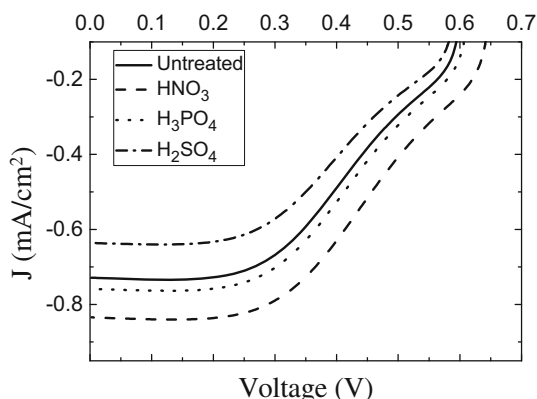
Table 1 Photoelectrochemical parameters of DSSCs sensitized by Trigonella seeds dye

Solvent	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Alcohol	0.371	0.599	48	0.106
Water	0.747	0.601	48	0.215

water, which means that the raise in efficiency from $\eta = 0.106\%$ with alcohol up to $\eta = 0.215\%$ with water leading to 202.8% improvement is due to the significant improvement in the short circuit current. It is worth mentioning that the extracts of water are different from those of alcohol. The current improvement can be attributed to the extracts of water.

Acidic treatment of FTO sheets

The DSSCs used in this treatment were sensitized with the natural extract of Trigonella seeds using water as a solvent. The J - V characteristic curves of DSSCs fabricated using untreated FTO (1st group) and those prepared using acid treated FTO (2nd, 3rd, and 4th groups) are plotted in Fig. 4. Their photoelectrochemical parameters are listed in Table 2. According to the J - V curves we can notice that the FTO treatment with HNO_3 and H_3PO_4 acids gave better performance than untreated cells. From Table 2, the treatment with HNO_3 gave a short circuit current $J_{sc} = 0.840$ mA/cm², $V_{oc} = 0.641$ V, and $\eta = 0.259\%$, leading to an improvement by 112.5, 106.6, and 120.4%, respectively, over the untreated cells. On the other hand, the enhancements in case of H_3PO_4 were only 101.2% for J_{sc} and 100.9% for V_{oc} . This improvement is due to better adhesion of the TiO_2 layer to the FTO, which means reducing the resistivity for high charge transport leading to higher short-circuit current density.

**Fig. 4** Current density–voltage curves for the DSSCs sensitized by Trigonella using untreated and acid treated FTO substrates**Table 2** Photoelectrochemical parameters of the DSSCs sensitized by Trigonella using untreated and acid treated FTO substrates

Acid	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
No-treatment	0.747	0.601	48	0.215
HNO_3	0.840	0.641	48	0.259
H_3PO_4	0.756	0.607	49	0.226
H_2SO_4	0.638	0.580	48	0.179

Impedance spectroscopy measurements

The solar cells sensitized with the extract of Trigonella seeds were perturbed by a small AC voltage signal of amplitude 10 mV with varying frequency (100 Hz to 200 kHz), to carry out an EIS study. This EIS study was employed to figure out the charge transport kinetics through the analysis of the Nyquist and Bode plots shown in Figs. 5 and 6, respectively. The main parameters calculated from the curves are the charge recombination resistance R_S , the charge transfer resistance R_{CT} , double layer capacitance (C_{dl}), the constant phase element CPE (α) due to double layer capacitance, and the effective lifetime of electrons τ . All these parameters were calculated and summarized in Table 3. As can be seen from the table, $R_S = 31\ \Omega$ which is small enough for fast electron transport, in the same context a very large $R_{CT} = 7,204\ \Omega$ indicates long lifetime (62.5 ms) for the electrons in the film. The CPE coefficient $\alpha = 0.76$ illustrates electrode surface roughness accompanied with complicated structure double layer capacitance.

Conclusions

The extract of Trigonella seeds as a natural sensitizer was used in the preparation of DSSCs. Two different solvents (alcohol and water) were used in the extraction process of

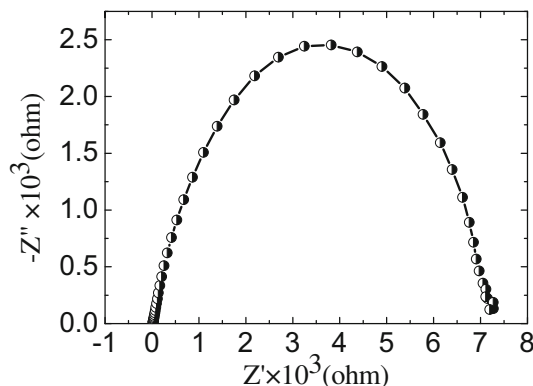
**Fig. 5** EIS Nyquist plots of DSSCs sensitized by Trigonella under an illumination of 100 mW/cm² and applied voltage of -0.7 V

Fig. 6 Bode plots of DSSCs sensitized by Trigonella under an illumination of 100 mW/cm² and applied voltage of -0.7 V

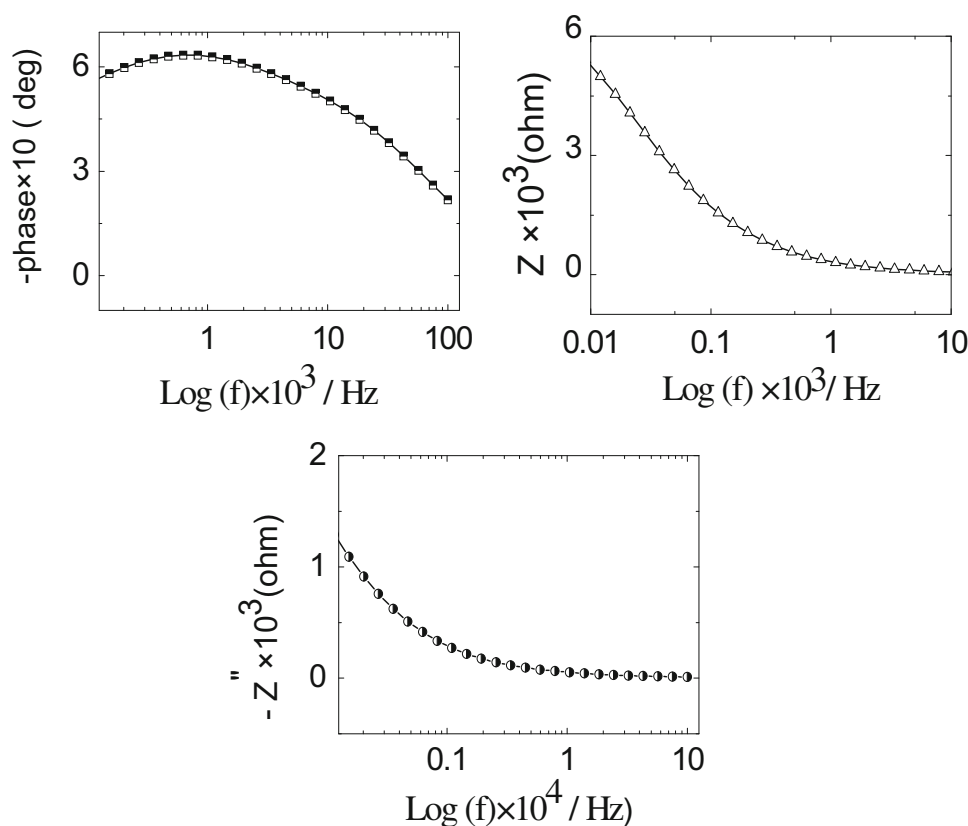


Table 3 The impedance spectroscopy parameters of the DSSCs sensitized by Trigonella

R_S (Ω)	R_{CT} (Ω)	C_{dl} (μF)	α (CPE coefficient)	τ (ms)
31	7,204	8.676	0.76	62.5

the dye from the raw material. The highest conversion efficiency of 0.215 % (with water as a solvent) compared to 0.106 % (with alcohol as a solvent) was obtained for the fabricated DSSC. A pre-treatment process for the FTO glass substrates with acidic solutions led to an efficiency improvement in case of HNO₃ and H₃PO₄. Impedance spectroscopy study for the fabricated solar cells was obtained from the analysis of the Nyquist and Bode plots, and the most important parameters like charge recombination resistance R_S , charge transfer resistance R_{CT} , constant phase element CPE due to double layer capacitance (C_{dl}), and effective lifetime of electrons τ were determined.

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