Dyes Extracted from Biota Orientalis, Piper Nigrum, and Glycyrrhiza glabra as Photosensitizers for Dye-Sensitized Solar Cells

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Abstract- Three natural dyes were extracted from Biota orientalis, Piper nigrum and Glycyrrhiza glabra and used as photosensitizers for dye-sensitized solar cells (DSSCs). The dyes were tested as sensitizers before and after grinding the materials. Titanium dioxide (TiO_2) nanopowder was used as a semiconducting material. The best photovoltaic performance was obtained for the DSSC sensitized with Glycyrrhiza glabra after grinding the material. This performance was significantly improved by acid treatment of the TiO_2 photoelectrode. Electrochemical impedance spectroscopy of the fabricated DSSCs was carried out and charge recombination resistance, double layer capacitance, effective lifetime of electrons, charge transfer resistance, and constant phase element exponential coefficient were determined.

Keywords: dye-sensitized solar cells, natural dyes, impedance spectroscopy, acid treatment.

1. Introduction

Solar energy is the one of the most interesting type of renewable energy sources because it can be converted to many other forms of energy. Producing electricity from sunlight using solar cells is developing rapidly according to its vital role in human life. A dye-sensitized solar cell (DSSC) is a device that converts visible light power into electricity, mimicking the photosynthesis operation in plants and has widely known as a low-cost, a friend of the environment and easy assembly solar cell. This promising solar cell was firstly developed by Grätzel's group [1-2]. A DSSC consists of two FTO transparent conducting glass electrodes in a sandwich arrangement [3,4]. The FTO anode electrode is coated by a layer of a nanocrystalline wide band gap semiconductor oxide such as TiO_2, SnO_2, ZnO,..etc, anchored by dye molecules that are employed as a photosensitizer. When the dye is excited by absorbing solar light photons, the excited electrons are injected into the conduction band of the semiconductor producing an electric current in the cell. The current travels through the external wire toward a platinum counter electrode (cathode). Between the two sandwiched FTO electrodes, a liquid electrolyte containing suitable redox couples (e.g. I_3^-/I^-) layer acts as a source for electron replacement, by compensating an electron to the ground state of the excited dye. The oxidized electrolyte is then reduced by receiving an electron from the bottom counter electrode layer.

There are a set of significant parameters that determine the light-to-electricity conversion efficiency of DSSCs such as the absorption spectrum of the dye extract, the position of the conduction band of the semiconductor relative to the excited state of the dye and the anchorage of the dye molecules to the surface of the semiconductor porous layer [5]. In general the photosensitizers used in DSSCs can be divided according to the dye structure into two types: inorganic dyes (metal complex, such as polypyridyl complexes of ruthenium and osmium) and organic dyes (natural and synthetic organic dyes). Although ruthenium polypyridyl complexes give the highest efficiency due to their high absorption of visible light, good chemical nature of converting light into electricity and stability of excitation states, they contain a heavy precious metal, which is undesirable for environmental and commercial aspects. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency [6]. The advantages of these dyes including their availability and low cost, turn the attention toward natural dyes. A large number of natural pigments can be easily extracted from several parts of the plant such as flowers, leaves, and seeds and then employed as photosensitizers in DSSCs [7-14]. The green leaves are rich in chlorophyll which has been investigated in many previous works [10,11]. The anthocyanin based dyes were also extensively studied [13]. Anthocyanin can be extracted from red cabbage, carrots and blackberries and it is responsible for the red and purple colors.

Impedance spectroscopy is an efficient experimental technique used for the study of electrochemical systems such as DSSCs. Because of the complexity of the DSSC network, the published impedance models describing their behavior are restricted to certain working conditions [15,16]. In this work the general features of impedance spectroscopy of the fabricated dye-sensitized solar cells will be discussed.

In this work, the extracts of Biota orientalis, Piper nigrum and Glycyrrhiza glabra were used as photosensitizers for DSSCs. The absorption spectra of the extracts of Biota orientalis, Piper nigrum and Glycyrrhiza glabra in ethyl alcohol solution were measured using a UV-VIS spectrophotometer. The natural dyes were tested as sensitizers before and after grinding the materials. The DSSCs were assembled using FTO conductive glass sheets as substrates and TiO_2 nanopowder as a semiconducting material. The current-voltage characteristics of the cells were measured to determine the photovoltaic parameters such as the conversion efficiency. The TiO_2 layer was treated by HCl or H_3PO_4 acids to improve the DSSC performance. Impedance spectroscopy of the fabricated DSSCs was studied and Nyquist and Bode curves were presented. The equivalent circuit of the fabricated DSSC was determined.

2. Experimental

2.1. Extraction of natural dye sensitizers

The natural dyes used in this study were extracted from the following plants: Biota orientalis, Piper nigrum and Glycyrrhiza glabra. The raw natural materials were first washed with distilled water, and then dried at 70 °C. The process of dye extraction was carried out before and after grinding the dyes so that two extracts were obtained for each dye: one was obtained before grinding and the other after grinding. 1 gm from each material (before grinding) were immersed in 5 ml ethyl alcohol at room temperature and in dark for one day. Another amounts of the dried materials were grinded into fine powder in a mortar. 1 gm from each material powder were immersed in 5 ml ethyl alcohol at room temperature and in dark for one day. After filtration of the solutions, natural dyes were obtained. Dye solutions were protected from direct light exposure.

2.2. Preparation of dye sensitized solar cells

FTO conductive glass sheets were cut into pieces of dimensions 0.8 cm×1.6 cm. The samples were cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. The TiO_2 paste was prepared by grinding equal weights of TiO_2 nanopowder and polyethylene glycol in a mortar for half an hour until a homogeneous paste was obtained. Thin layers of the prepared TiO_2 paste were spread on the transparent conducting FTO coated glass by employing doctor blade method with an effective area of 0.5cm×0.5cm. Samples were then dried in an oven at 70 °C for 20 min. Finally, the samples were sintered at 450 °C for 40 min then cooled down to 70 °C before being placed in dye solutions for one day under dark. The DSSC was then assembled by pressing the dyed TiO_2 electrode and the platinum counter electrode together and clamping them firmly in a sandwich configuration. The electrolyte redox (I^-/I_3^-) was spread within the vicinity between the two electrodes. The photovoltaic properties of the fabricated cells were investigated.

To investigate the effect of the acid post-treatment of TiO_2 film on the DSSC performance, another group of the prepared TiO_2 films, were soaked in 0.1 M HCl or H_3PO_4 acids at room temperature for 5 min. The acid treated TiO_2 films were then washed with ethanol. The DSSCs were then assembled as described above.

2.3. Characterization and measurement

The UV–VIS absorption spectra of the extracts of Biota orientalis, Piper nigrum and Glycyrrhiza glabra in ethyl alcohol solution were measured using a UV-VIS spectrophotometer (Thermoline Genesys 6). The wavelength range of absorption spectra analysis was taken from 400−850 nm.

The current density-voltage (J-V) characteristic curves of the fabricated DSSCs were measured using National Instruments data acquisition card (USB NI 6251) in combination with 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. The J-V curves were measured at 100 mW/cm^2 irradiations using high pressure mercury arc lamp.

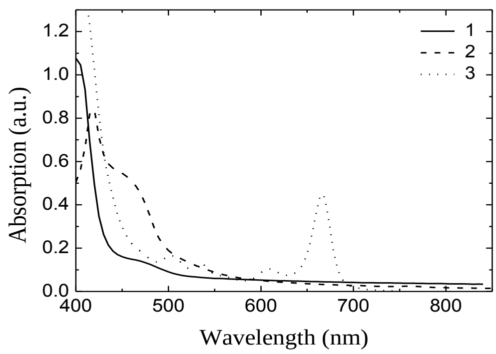

Fig. 1. Light absorption spectra of the extract of (1) Biota orientalis, (2) Piper nigrum and (3) Glycyrrhiza glabra.

3. Results and Discussions

3.1. Absorption spectra

The UV–VIS absorption spectra of Biota orientalis, Piper nigrum and Glycyrrhiza glabra in ethyl alcohol as a solvent are shown in Fig. 1. It can be seen from the figure that there are absorption peaks at about 400 nm and 430 for the extract of Biota orientalis. The absorption spectrum of piper nigrum shows a peak at 404 nm, a shoulder at 410 nm and a peak at 455 nm. The extract of Glycyrrhiza glabra shows a set of peaks with a significant one at 665 nm.

Diffuse reflectance spectra were collected with a V-670, JASCO spectrophotometer and transformed to the absorption spectra according to the Kubelka-Munk relationship. The absorption spectra of the solutions of the three extracts of Biota orientalis, Piper nigrum and Glycyrrhiza glabra and those of the TiO_2 electrode after being soaked in the three extracts are shown in Fig. 2. As can be seen from the three panels of Fig. 2, the absorption bands of dye/TiO_2 is red shifted towards higher wavelength compared to that of the extracts in solutions. As examples of the red shift obtained, the Biota orientalis dyed film has a peak at 414 nm instead of that at 400 nm for Biota orientalis solution, the Piper nigrum dyed film has a peak at 420 nm instead of 404, and the Glycyrrhiza glabra dyed film has a peak at 676 nm instead of 665 nm. The observed hyperchromic shift is typical for adsorbed dyes on solid substrates.

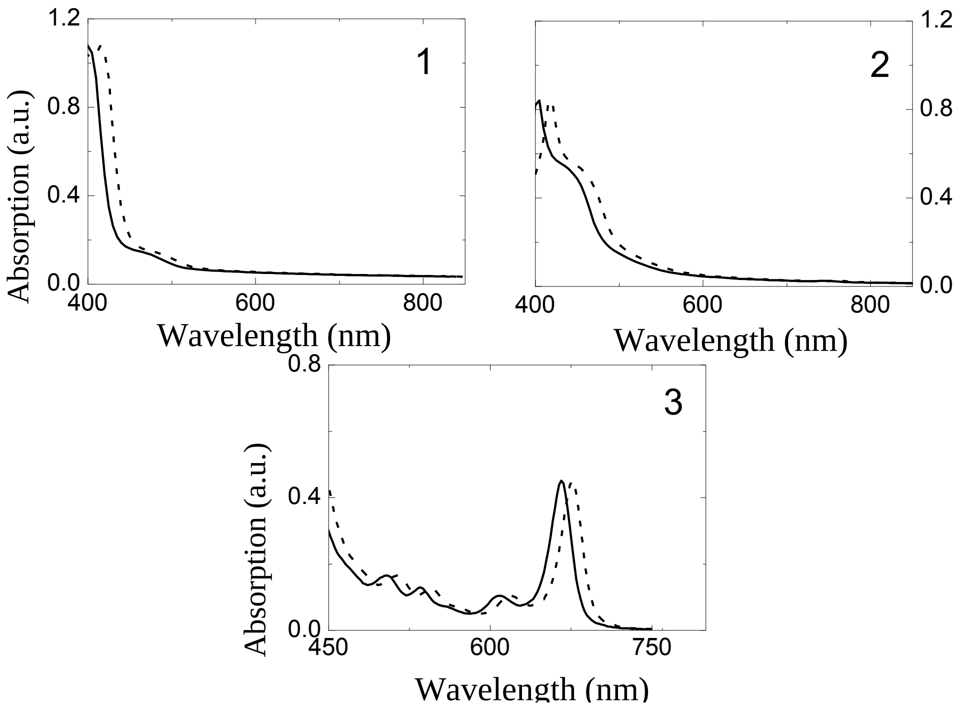

Fig. 2. Light absorption spectra of dye solutions (solid lines) and dyes adsorbed on TiO_2 (dashed lines) for (1) Biota orientalis, (2) Piper nigrum and (3) Glycyrrhiza glabra.

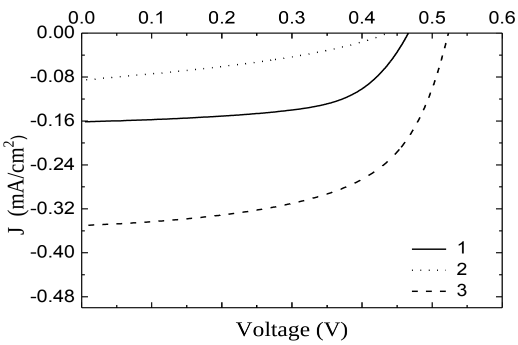

Fig. 3. Current density–voltage curves for the DSSCs sensitized by (1) Biota orientalis, (2) Piper nigrum and (3) Glycyrrhiza glabra, before grinding.

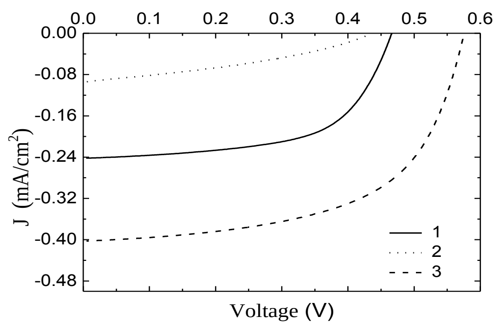

Fig. 4. Current density–voltage curves for the DSSCs sensitized by (1) Biota orientalis, (2) Piper nigrum and (3) Glycyrrhiza glabra, after grinding.

3.2. Photovoltaic properties

The performance of the natural sensitizers in the photoelectrochemical solar cells was examined through electrical current and voltage outputs under 100 mW/cm^2 illuminations. Figures 3 and 4 show the J-V characteristic curves of the DSSCs sensitized with the three natural extracts before and after grinding. Table 1 presents all the photoelectrochemical parameters of the fabricated DSSCs sensitized with the three materials before and after grinding. These parameters include the short circuit current J_{sc}, open circuit voltage V_{oc}, fill-factor FF, and the conversion efficiency η. It is obvious from the table that the DSSCs sensitized with the extracts obtained from grinded materials exhibit better photovoltaic response. However, the FF shows an independence of the grinding process. It is clear from Table 1 that the DSSC sensitized with glycyrrhiza glabra shows the highest photoelectrochemical performance among the DSSCs with J_{sc} = 0.35 mA/cm^2, V_{oc} = 0.535 V, FF = 35%, and η = 0.042% before grinding and J_{sc} = 0.40 mA/cm^2, V_{oc} = 0.540 V, FF = 35%, and η = 0.050% after grinding. The efficiency improvement due to the grinding process is about 119%.

Table 1. Photoelectrochemical parameters of the DSSCs sensitized by the three extracts of Biota orientalis, Piper nigrum and Glycyrrhiza glabra, before and after grinding.

Natural dye	J_{sc} (mA/cm^2)		V_{oc} (V)		FF(%)		η(%)	
	before	after	before	after	before	after	before	After
Biota orientalis	0.160	0.240	0.460	0.465	30	29	0.018	0.022
Piper nigrum	0.080	0.090	0.425	0.430	20	20	0.008	0.009
Glycyrrhiza glabra	0.350	0.400	0.535	0.540	35	35	0.043	0.050

3.3. Impedance spectroscopy measurements

Electrochemical impedance spectroscopy (EIS) study was carried out in order to study the charge transport kinetics in the cell [17]. During the EIS study, the DSSC was perturbed by a small AC voltage signal of amplitude 10 mV with varying frequency (10 mHz – 10 MHz). According to the DSSC response, the Nyquist and Bode curves show that the suitable equivalent circuit can be plotted as illustrated in Fig. 5 in which R_S is the charge recombination resistance, CPE is the constant phase element due to double layer capacitance (C_{dl}), and R_{CT} is the charge transfer resistance. Figure 6 illustrates Nyquist curves for the DSSCs sensitized by Biota orientalis, Piper nigrum and Glycyrrhiza glabra whereas Fig. 7 shows Bode modulus curves for the DSSCs sensitized by the three extracts. From Figs. 6 and 7, the charge recombination resistance R_S, the double layer capacitance C_{dl}, effective lifetime of electrons τ, the charge-transfer resistance R_{CT}, and the CPE exponential coefficient α can be estimated. The values of R_S, R_{CT}, C_{dl}, α, and τ obtained from the Nyquist and Bode plots are presented in Table 2. From these results we can conclude that for the DSSC sensitized by Biota orientalis $R_{CT}>>R_S$ which indicates fast electron transport and long lifetime of electrons in the film. In the case of the DSSC sensitized by Piper nigrum $R_S>R_{CT}$ which means that a major part of the electrons reacts with I_3^- in the electrolyte before they are recovered at the collected current. On the other hand, the DSSC sensitized with Glycyrrhiza glabra shows nearly equal values of recombination and transfer resistances, which means that it has a carrier collection efficiency near unity. The values of the CPE coefficient (α) for Biota orientalis and Piper nigrum correspond to diffusion with deviations and surface roughness. High α value as in the DSSC sensitized with Glycyrrhiza glabra adds the probability of complicated structure in the double layer capacitor.

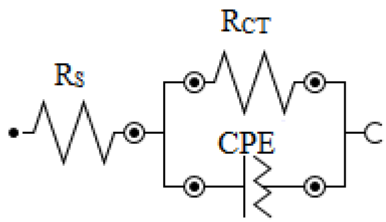

Fig. 5. The equivalent circuit for the DSSCs sensitized by natural dyes extracted with ethyl alcohol as solvent.

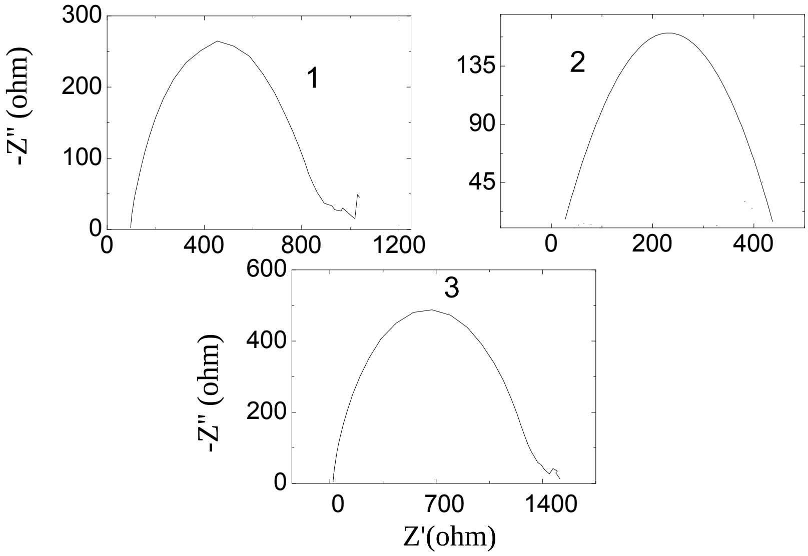

Fig. 6. Nyquist curves for the DSSCs sensitized by (1) Biota orientalis, (2) Piper nigrum and (3) Glycyrrhiza glabra.

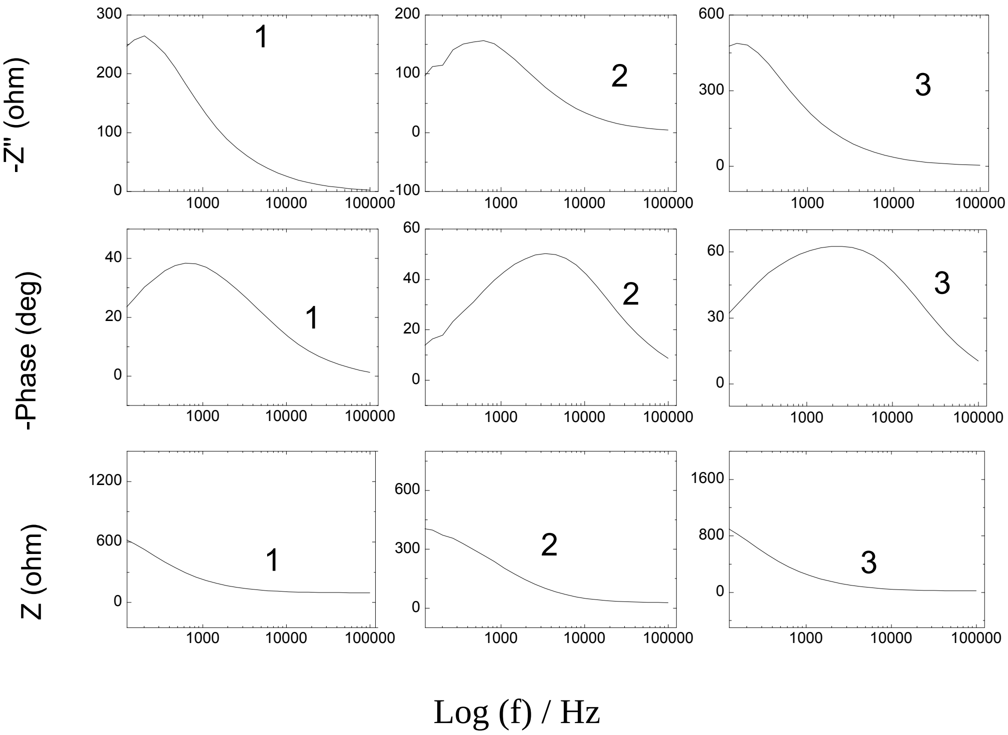

Fig. 7. Bode modulus curves for the DSSCs sensitized by (1) Biota orientalis, (2) Piper nigrum and (3) Glycyrrhiza glabra.

Table 2. The impedance spectroscopy parameters of the DSSCs sensitized by the extracts of Biota orientalis, Piper nigrum and Glycyrrhiza glabra.

Natural dye	R_S (Ω)	R_{CT} (Ω)	C_{dl} (μF)	α (CPE coefficient)	τ (ms)
Biota orientalis	99	850	26.7	0.7	22
Piper nigrum	1870	889	5.25	0.56	4.6
Glycyrrhiza glabra	930	883	8.78	0.8	7.7

3.4. Photovoltaic properties after acidic treatment

The J-V characteristics of untreated DSSCs and those with acid treated TiO_2 electrodes were tested under 100 mW/cm^2 intensity. Their photoelectrochemical parameters are summarized in Table 3. The acid treatment showed reduced V_{oc} values for DSSCs sensitized with Biota orientalis, almost the same V_{oc} values for DSSCs sensitized with Piper nigrum, and enhanced V_{oc} values for DSSCs sensitized with Glycyrrhiza glabra. Acid treated DSSCs showed a noticeable improved short circuit current density and a considerable enhanced overall conversion efficiency in comparison with untreated DSSCs. The DSSC sensitized with Biota orientalis showed an efficiency enhancement of about 336% with HCl treatment and 400 % with H_3PO_4 treatment whereas that sensitized with Piper nigrum exhibited an efficiency improvement of about 211% with HCl treatment and 188 % with H_3PO_4 treatment. The cell sensitized with Glycyrrhiza glabra showed an efficiency enhancement of about 300% with HCl treatment and 290 % with H_3PO_4 treatment. The highest enhancement was obtained with H_3PO_4 acid treatment of the cell dyed with Biota orientalis whereas the highest conversion efficiency of 0.15% was obtained for the DSSC dyed with Glycyrrhiza glabra and treated with HCl. The acid treatment efficiency improvement may be attributed to the acid contributed regular arrangement of the photoelectrode via the dispersion of TiO_2 particles. This dispersion is considered one of the most important factors that make much chemisorption site for the organic dyes. Moreover, the acid treatment is believed to improve the neck points between the TiO_2 nanoparticles which provides an improved electrical conductivity leading to reduced recombination.

Table 3. Photoelectrochemical parameters of the untreated and acid treated DSSCs.

Natural dye	J_{sc} (mA/cm^2)			V_{oc} (V)			η (%)		
	Untreated	HCl	H_3PO_4	untreated	HCl	H_3PO_4	untreated	HCl	H_3PO_4
Biota orientalis	0.240	0.265	0.315	0.465	0.445	0.447	.022	0.074	0.088
Piper nigrum	0.090	0.124	0.113	0.430	0.433	0.432	.009	0.019	0.017
Glycyrrhiza glabra	0.400	0.451	0.437	0.540	0.574	0.573	.050	0.150	0.145

4. Conclusions

The extracts of Biota orientalis, Piper nigrum, and Glycyrrhiza glabra were tested as natural sensitizers for DSSCs. These dyes were used as photosensitizers before and after grinding the materials. The highest conversion efficiencies of 0.042% (before grinding) and 0.050% (after grinding) were obtained for the DSSC sensitized with Glycyrrhiza glabra. The grinding process leaded to an efficiency improvement of about 119%. The performance of the fabricated DSSCs was considerably enhanced by the treatment of the TiO_2 photoelectrode by HCl and H_3PO_4 acids. An efficiency improvements of about 336% and 400 % were obtained with HCl and H_3PO_4 treatments of the DSSC sensitized with Biota orientalis. The DSSC sensitized with Piper nigrum showed an efficiency enhancement of about 211% with HCl treatment and 188 % with H_3PO_4 treatment whereas the cell sensitized with Glycyrrhiza glabra exhibited efficiency improvements of 300% and 290% with HCl and H_3PO_4 treatments, respectively. The conversion efficiency enhancement obtained with H_3PO_4 acid treatment of the DSSC

sensitized with Biota orientalis was the highest improvement. The highest efficiency of 0.15% was obtained for the DSSC sensitized with Glycyrrhiza glabra after treating the TiO_2 photoelectrode with HCl acid.
Impedance spectroscopy of the fabricated DSSCs was studied and Nyquist and Bode curves were plotted. The DSSC equivalent circuit was obtained and its parameters such as charge recombination (R_S) and charge transfer (R_{CT}) resistances were determined.

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