

Dye-Sensitized Solar Cells Using Dyes Extracted From Flowers, Leaves, Parks, and Roots of Three Trees

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Received: 17.12.2014 Accepted: 22.02.2015

Abstract- In this paper, eleven natural dyes were collected from three trees and used as photosensitizers for dye sensitized solar cells (DSSCs). The cells were fabricated using TiO₂ as a semiconducting layer deposited on transparent fluorine doped tin oxide (FTO) conductive glass using doctor blade method. The absorption spectra of the extracts were performed in the spectral range from 400 nm to 750 nm. The J-V characteristic curves of all fabricated cells were measured and analyzed. The parameters related to the solar cell performance were determined. Moreover, the impedance spectroscopy of the cell with the best performance was investigated.

Keywords- Renewable energy, dye-sensitized solar cells, natural dyes, TiO₂.

1. Introduction

Grätzel was the first who investigated dye-sensitized solar cells (DSSCs) as a new type of solar cells in 1991 [1]. Since that time, DSSCs have received an increasing interest [2-16] due to many advantageous over other types. A DSSC is formed of a nanocrystalline metal oxide semiconducting layer deposited on transparent fluorine doped tin oxide (FTO) conductive glass, adsorbed dye on the semiconducting material, counter electrode, and an electrolyte containing iodide and triiodide ions. In DSSCs, the adsorbed dye behaves as a sensitizer for absorbing sunlight. The conversion of solar energy into electricity in solar cells is based on charge separation. In silicon cells, an absorbed photon makes free an electron-hole pair, and the charge separation is calculated by an electric potential difference. Silicon solar cell is expensive and its efficiency is highly affected when the illumination is low. DSSCs have many advantages over silicon solar cells. They are cheaper, there is no need for clean room technology, and the efficiency in low light conditions is not highly affected. The technology of DSSCs is not yet mature and a lot of research is still needed.

The use of natural dyes extracted from trees, fruits, and vegetables as sensitizers for the conversion of solar energy

into electricity is very interesting because it improves the economical aspect and makes important profit from the environmental.

In this paper, eleven natural dyes were extracted from three trees and used as DSSC photosensitizers. Dyes were extracted from flowers, fruits, leaves, barks, and roots of olive, lycium shawii, and zizyphus trees. The absorption spectra of these dyes were carried out. The J-V characteristic curves of all fabricated cells were measured, plotted, and analyzed.

2. Experiment

Eleven natural dyes were collected from three trees. These trees are olive, lycium shawii, and zizyphus. One dye was extracted from the flowers of lycium shawii, one dye was taken from the grain of olive, three dyes were extracted from the leaves of the three trees, three dyes were extracted from their barks, and three dyes were extracted from their roots. The raw materials were washed with distilled water and left to dry at room temperature for about a week. After drying and crushing into fine powder using a mixer, 200 mg of each powder was immersed in 5 ml of ethanol at room temperature in dark for one day. The extracts were then obtained. They were filtered out to remove the remaining

solids of the powders. UV-VIS spectrophotometer (Thermoline Genesys 6) was used to carry out the absorption spectra of the extracts in the visible range.

FTO conductive glass sheets (Xingyan Tech. Ltd, Hong Kong) were used as substrates. TiO₂ paste was prepared by adding 50 mg of TiO₂ nanopowder to 100 mg of polyethylene glycol then grinding the mixture for half an hour until a homogeneous paste was obtained. The paste was deposited on the FTO substrates using doctor-blade method to obtain the TiO₂ film. The area of the TiO₂ layer was restricted to 0.25 cm². The TiO₂ layer was sintered in an oven at 450 °C for 40 min. The films were left in the oven to cool down slowly to 60 °C. The thickness of the TiO₂ layer was measured using Olympus Polarizing Microscope BX53-P equipped with DP73 camera, and found to be 21±1 μm. The TiO₂ films were then immersed in the natural extracts for one day [2].

The cells were assembled by fixing the working electrode and the counter electrode by paper clips with a spacer between the electrodes. The redox electrolyte solution was composed of 2 mL acetonitrile (ACN), 8 mL propylene carbonate (p-carbonate), 0.668 mg potassiumiodide (KI), and 0.0634 mg iodine (I₂). The redox electrolyte solution was sandwiched between the two electrodes.

After illumination of the DSSCs with 100 mW/cm² irradiation using a high-pressure mercury arc lamp, National Instruments data acquisition card (USB NI 6251) was used to conduct the current-voltage curves of the fabricated cells. The measurements were conducted using LabVIEW program.

Impedance spectroscopy was conducted to find out the equivalent circuit of the fabricated cells. Impedance spectroscopy was conducted using a Potentiostat-galvanostat Autolab PGSTAT-30N with FRA32M module. In the measurement of electrochemical impedance, the user generates a sine wave with known parameters. The AC signal is applied to the cell. In our work, the imposed AC signal had amplitude of 0.6 V and frequency in the range from 0 and 100 KHz. The AC voltage and current components are analyzed by the two FRA channels and the transfer function. The real and imaginary parts of the impedance are calculated. Moreover, the phase angle shift is also determined. After analyzing the results, the equivalent circuit of the DSSC can be found. All measurements were performed with the NOVA software. The impedance was measured and plotted to obtain Nyquist and Bode plots. The equivalent circuit has been derived from the rate of electron transfer and lifetime of the electron in the film, which are consistent with the values derived from the transient photocurrent and photovoltage measurements [8].

3. Results and Discussion

The solar cell parameters of interest are short circuit current density (J_{sc}), open circuit voltage (V_{oc}), wavelength at the absorption curve peak (λ_{max}), maximum power point (P_{max}), fill factor (FF), and efficiency (η). The wavelength of maximum absorption of the extract is determined from absorption spectra curves. The short circuit current density and open circuit voltage are obtained from the J-V curves by estimating the J- and V- axes intersections, respectively. The maximum power point is determined from the P-V curves from which I_{MP} and V_{MP} can be calculated. The fill factor and efficiency are calculated using

$$FF = \frac{I_{MP} V_{MP}}{I_{SC} V_{OC}}, \quad (1)$$

and

$$\eta = \frac{FF I_{SC} V_{OC}}{P_{in}}, \quad (2)$$

where P_{in} is the power of incident light.

The absorption spectra of two extracts are plotted in Fig. 1. The figure shows that there are well defined absorption peaks at about 660 nm for both extracts of lycium shawii and zizyphus leaves, a characteristic absorption spectrum of chlorophyll a. The figure also shows wide absorption bands in the region from 400-500 nm, which may be attributed to a combined absorption of the chlorophyll Soret bands as well as the presence of quantities of carotenoids co extracted with the pigment. Values of the maximum absorption wavelength of the tested natural pigments are listed in Table 1.

The J-V measurements have been conducted under illumination of 100 mW/cm² using high pressure mercury arc lamp equipped with an IR filter. Figure 2 illustrates the variation of the current density with the voltage for the DSSCs sensitized with lycium shawii and zizyphus leaves. All J-V characteristic curves are found to have the shape of diode's characteristic curve. All the photoelectrochemical parameter of the fabricated cells can be calculated from the J-V characteristic as presented in Table 1. As can be seen from the table, the short circuit current varied from 0.13 mA/cm² to 1.50 mA/cm². The highest short circuit current was obtained for the DSSC sensitized with zizyphus leaves and the lowest short circuit current was obtained for the DSSC sensitized with lycium shawii root. The open circuit voltage ranged from 0.38V for the DSSC sensitized with lycium shawii root to 0.68V for the DSSC sensitized with zizyphus leaves. The maximum output power of the fabricated cells varied from 0.01 mW/cm² for the DSSC sensitized with lycium shawii root to 0.40 mW/cm² for the DSSC sensitized with zizyphus leaves. On the other hand,

the FF ranged from 0.24 for the DSSC sensitized with lycium shawii root to 0.43 for the DSSC sensitized with lycium shawii leaves. The highest conversion efficiency was 0.40 for the DSSC sensitized with zizyphus leaves. Generally, the DSSCs sensitized with plant leaves exhibited high efficiency compared to those sensitized with roots and barks in which the efficiency was extremely low.

These values for the cell parameters are relatively comparable to the values obtained in many previous works based on natural dyes such as Refs. 9 and 10. In Ref. 9, DSSCs were fabricated using natural extracts from black rice, capsicum, erythrina variegata flower, rosa xanthina, and kelp. The reported values were: J_{SC} from 0.225 mA/cm² to 1.142 mA/cm², V_{OC} from 0.412 V to 0.551 V, and FF from 0.52 to 0.63. In Ref. 10, twenty natural dyes extracted from natural materials such as flowers and leaves were used as sensitizers for DSSCs. The photoelectrochemical performance of the DSSCs based on these dyes showed V_{OC} and J_{SC} in the ranges 0.337 - 0.689 V and 0.14 - 2.69 mA/cm², respectively.

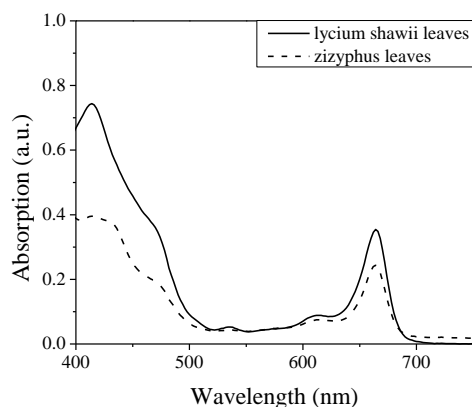


Fig. 1. Absorption spectra of lycium shawii and zizyphus leaves using ethanol as a solvent.

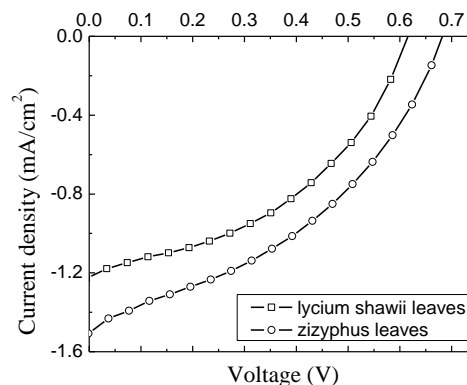


Fig. 2. J-V characteristic curves of the DSSCs sensitized with lycium shawii and zizyphus leaves.

Since the DSSC sensitized with zizyphus leaves exhibited the best performance, it was investigated using impedance spectroscopy. Figure 3 shows Nyquist Plot, Bode plot, and the equivalent circuit of the DSSC dyed with the extract of Zizyphus leaves. The low fill factor of the fabricated DSSCs (0.24 - 0.43) can be explained based on the results of the equivalent circuit. It arises from the large series resistance and the low shunt resistance in the cells as shown in the equivalent circuit. Series resistance may be attributed to ohmic resistance and poor connection between material interfaces. Moreover, low mobility of the electrolyte can contribute to the series resistance. Low shunt resistance indicates that the current has alternative ways of crossing the cell other than the desired one, e.g. if the TiO₂ electrode is in almost direct contact with counter electrode.

Table 1. The parameters of the fabricated DSSCs.

| Extract | λ_{Max} (nm) | J_{SC} (mA/cm ²) | V_{OC} (V) | J_{MP} (mA/cm ²) | V_{MP} (V) | P_{Max} (mW/cm ²) | FF | η % |
|----------------------|----------------------|--------------------------------|--------------|--------------------------------|--------------|---------------------------------|------|----------|
| lycium shawii flower | 662 | 0.42 | 0.58 | 0.38 | 0.27 | 0.10 | 0.42 | 0.10 |
| olive grain | 666 | 0.58 | 0.55 | 0.38 | 0.31 | 0.12 | 0.38 | 0.12 |
| olive leaves | 432 664 | 0.85 | 0.59 | 0.35 | 0.48 | 0.17 | 0.33 | 0.17 |
| lycium shawii leaves | 412 664 | 1.20 | 0.62 | 0.39 | 0.82 | 0.32 | 0.43 | 0.32 |
| zizyphus leaves | 416 662 | 1.50 | 0.68 | 0.43 | 0.93 | 0.40 | 0.40 | 0.40 |
| olive bark | 662 | 0.35 | 0.54 | 0.34 | 0.18 | 0.06 | 0.32 | 0.06 |
| lycium shawii bark | 434 662 | 0.15 | 0.44 | 0.26 | 0.07 | 0.02 | 0.29 | 0.02 |
| zizyphus bark | 662 | 0.42 | 0.50 | 0.30 | 0.24 | 0.07 | 0.35 | 0.07 |

| | | | | | | | | |
|--------------------|-----|------|------|------|------|------|------|------|
| olive root | 636 | 0.45 | 0.53 | 0.30 | 0.28 | 0.08 | 0.35 | 0.08 |
| lycium shawii root | 662 | 0.13 | 0.38 | 0.22 | 0.06 | 0.01 | 0.26 | 0.01 |
| zizyphus root | 664 | 0.37 | 0.49 | 0.26 | 0.16 | 0.04 | 0.24 | 0.04 |

It is worth mentioning that the response of the fabricated cells can be improved by adjusting the pH of the natural dye solution using acetic acid. It was reported that the acetic acid may promote bonding between the hydroxyl groups of natural dyes and the surface of the nanocrystalline-TiO₂ film [16]. Sensitizing dyes adsorbed on TiO₂ surfaces are known to be desorbed by addition of bases (NaOH, NH₃, etc.) [16]. Thus, the photovoltaic improvement upon addition of acetic acid is possibly attributable to a difference in dye adsorption modes: chemical bonding adsorption mode (with acetic acid) and physical (van der Waals) adsorption mode (without acetic acid) [16].

4. Conclusion

Eleven natural dyes were extracted from three trees and used as photosensitizers for DSSCs. These dyes were extracted from the leaves, flowers, barks, and roots of the three trees. TiO₂ was used as a semiconductor. DSSCs sensitized with plant leaves showed higher efficiency than those sensitized with other parts of the trees due to the presence of chlorophyll a as the absorption spectra showed. The highest conversion efficiency was 0.40% for the DSSC sensitized with zizyphus leaves. DSSCs sensitized with roots and barks exhibited the lowest response.

Acknowledgement

The authors would like to express gratitude to the ministry of higher education for the financial support of this work.

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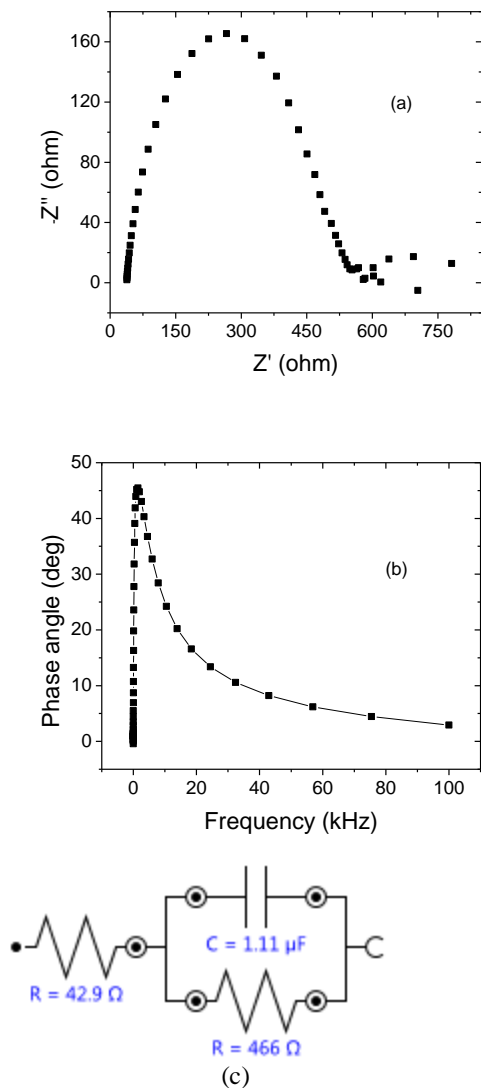


Fig. 3. Output of impedance spectroscopy for the DSSC sensitized with the extract of zizyphus leaves (a) Nyquist Plot, (b) Bode plot, and (c) equivalent circuits.

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