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Low cost dye-sensitized solar cells based on zinc oxide and natural anthocyanin dye from *Ardisia elliptica* fruits

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ABSTRACT

Natural dye is attractive to be used in dye sensitized solar cell (DSSC) as an alternative sensitizer. The main advantage of natural dye is its low cost production. Only simple procedure is needed to produce natural dyes where the pigments of plant parts like flowers, leaves, fruits and tubers were extracted using common solvents in the laboratory. In addition, the resources of natural dye are not only abundant, but also completely biodegradable. In this work, the natural dye was produced by extracting anthocyanin pigment from *Ardisia elliptica* fruits and called as *Ardisia elliptica* dye (AED). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level of AED was −6.06 eV and −3.88 eV respectively. AED is absorbed light in the green region with maximum absorption at a wavelength of 536.49 nm and the band gap was 2.31 eV which is acceptable as sensitizer for DSSC. Our photoelectrode of DSSC was fabricated by sensitizing zinc oxide (ZnO) nanoparticles layer with AED in different sensitizing duration (dye-loading time) and the best obtained photo conversion efficiency (PCE) was 0.04% which has been sensitized for 20 min.

1. Introduction

Research work related to dye-sensitized solar cell (DSSC) is increasingly reported and is one of the intense topic in the solar energy field. It is motivated by the cheaper materials and simple fabrication method of which makes the DSSC a promising means of solar energy conversion [1] after the silicon solar cell. It was pioneered by Grätzel's group in 1991 using sensitized titanium dioxide nanoparticles with a monolayer of trimeric ruthenium (Ru) complex [2]. Natural dye was reported as an alternative to Ru-based dye due to its eco-friendly characteristic and abundant in resources [3,4]. Natural dye is produced from the extraction of pigments from plants using common solvents i.e. acetone, distilled water, ethanol [5], and methanol [6,7]. Plant parts that have been reported in preparing natural dyes were leaf [8,9], flower [10,11], fruit [12,13] and tuber [14]. The reported pigment constituents in natural dye that have been applied in DSSC were anthocyanin [15,16], betalain [17], carotenoid [18] and chlorophyll [19–21].

Typically titanium dioxide (TiO_2) is used as metal oxide layer in DSSC for electron collection, however, several studies have reported applying zinc oxide (ZnO) as an alternative due to the fact that both TiO_2 and ZnO have same electron affinities and almost the same band gap energies, i.e., ~3.2 eV and ~3.3 eV, respectively. Furthermore, ZnO has much higher electron diffusivity [22] and

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excellent bulk electron mobility (115–155 $cm^2 V^{-1} s^{-1}$) [23] with larger in more than 1 order of magnitude than anatase TiO_2 [24] which could contribute to efficient electron transport in the semiconductor and for reduction of recombination rate. Here in, we reported the application of natural dye from *Ardisia elliptica* fruits in our ZnO-based DSSC and discussed about the dye-loading duration effect on the photovoltaic performances in our DSSCs. To the best of our knowledge, there is no research has been done in investigating the sensitization of ZnO with natural dye from *Ardisia elliptica* fruits so far in natural-DSSCs realm.

2. Experimental

2.1. Indium tin oxide glass cleaning and paste preparation

The conductive substrate of choice as electrodes in our DSSCs were indium doped tin oxide (ITO) glasses with resistivity of 10–12 Ω and dimension of 2 cm x 2 cm. The glasses were cleaned ultrasonically with distilled water, acetone (R&M Chemicals) and ethanol (95%, HmbG Chemicals), respectively in 5 min (min) for each step and lastly the ITO glasses were dried with a hair dryer. The ZnO paste was prepared by mixing 0.15 g of ZnO nanopowder (< 100 nm, Sigma Aldrich) in 0.5 ml of methanol (R&M Chemicals) and ultrasonically vibrated in a small vial.

2.2. The extraction of natural dye from Ardisia elliptica fruits

The natural dye was prepared by extracting anthocyanin pigments from *Ardisia elliptica* fruits hence, named as *Ardisia elliptica* dye (AED). The fruits were cleansed with tap water to remove dirt and rinsed thoroughly with distilled water several times. After that, the cleansed fruits were air dried in fume hood for a day to ensure all distilled water on fruits evaporated. The dried fruits were mixed with ethanol (95%, HmbG Chemicals) in a beaker with a ratio of 1:5. Then, the beaker was covered and heated at 40 °C for 2 h (h) on a hot plate for the extraction process. Finally, the dye solution was filtered to remove fruits residue and used without further purification.

2.3. Preparation of photoelectrode and counter electrode

The ZnO layer was fabricated on ITO glass using doctor blade technique. The ITO glass that has been deposited with ZnO layer were dried with hair dryer for a while before annealed at 450 °C for 10 min on a hot plate. The annealing step was important for enhancing the attachment of ZnO layer with ITO layer and also to remove solvent that would dampened the mobility of charge carrier in sample. After completing the annealing steps, the sample was left to cool down completely before dipped into AED solution for sensitization process. The sensitization process was carried out from 10 min–50 min with 10 min interval in a covered beaker and in the dark environment. After the sensitization completed, the sample was taken out and rinsed with ethanol several times. After that the sample was dried with hair dryer and called as photoelectrode. In the meantime, the counter electrode (CE) was prepared by scratching the conductive side of ITO glass with a pencil several times to deposit graphite on it as catalyst layer.

2.4. Fabrication of the DSSC

Our DSSC was fabricated by sandwiching the photoelectrode with CE and the gap between both electrodes was filled with a redox electrolyte containing 0.5 M lithium iodide (99.9% Sigma Aldrich) and 0.05 M iodine (Fluka Analytical) in acetonenitrile (Merck KGaA) [25].

2.5. Characterization of the DSSC

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level were studied through cyclic–voltammetry method [26] via Metrohm Autolab. In other hand, the optical properties of AED were determined by employing UV–vis spectrophotometer (Model Lambda 25 with UV Winlab V2.85 software, Perkim Elmer). Fourier-transform infrared (FTIR) spectroscopy (IRTracer-100, SHIMADZU) was used to investigate the chemical compounds exist in the AED while the photovoltaic parameters were collected from I–V measurement via potentiostat (Autolab PGSTAT30, Eco Chemie B.V., The Netherlands) employing NOVA software under illumination of 100 $mWcm^{-2}$ using xenon lamp.

3. Results and discussions

Energy level of materials in DSSC are crucial to match with each other in a fashion where the HOMO of dye must be lower than the redox level of electrolyte, and the LUMO should be sufficiently higher than the conduction band of metal oxide of choice. HOMO and LUMO level were determined by evaluating oxidation onset and reduction onset of C–V plot in Fig. 1. The C–V characterization was executed with platinum mesh and potassium chloride electrodes as counter and references electrodes, respectively. The electrochemical measurement were carried out with the scan rate of 0.05 V/s and step potential of 0.01 V. All measurement were done at room temperature and in the dark.

The HOMO and LUMO of AED were obtained via eq (1) and (2),where E_{HOMO} and E_{LUMO} represent energy level of HOMO and LUMO, respectively, while $E^{Onset}_{Oxidation}$ and $E^{Onset}_{Reduction}$ are the value of oxidation and reduction coordinates in C–V plot respectively and 4.4