

Full Length Research Paper

Dye sensitized solar cell using natural dyes extracted from red leave onion

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Extracts from red leave onion (*Allium cepa*) were used as natural sensitizers of a wide band-gap semiconductor (TiO₂) in photoelectrochemical solar cells. The natural dye, adsorbed onto the semiconductor surface, absorbs visible light and promotes electron transfer across the dye/semiconductor interface. Photogenerated current density and voltage as high as 0.85 mA m⁻² and 0.65 mV, respectively were obtained and effective energy conversion efficiency of 0.29% was achieved. These simple and cheap techniques of cell preparation therefore open up a perspective of commercial feasibility for inexpensive and environmentally friendly dye cells.

Key words: *Allium cepa*, band-gap, photoelectrochemical solar cell, natural dye, semiconductor.

INTRODUCTION

Owing to the rapid increase in the world energy demand, combined with the depletion of fossil resources, global warming and its associated climate change, there is an urgent need for environmentally sustainable energy technologies. Among all the renewable energy technologies, such as wind turbines, hydropower, wave and tidal power, solar cells, solar thermal, biomass-derived liquid fuels and biomass-fired electricity generation, photovoltaic technology utilizing solar energy is considered as the most promising one. Fortunately, the supply of energy from the sun to the earth is gigantic; 3×10^{24} J a year, or about 10,000 times more than that the global population currently consumes. In other words, covering 0.1% of the earth's surface with solar cells with an efficiency of 10% would satisfy our present needs (Huang et al., 1997).

To date, the field of photovoltaic has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells, based on nanocrystalline oxide. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry.

It is now possible to depart completely from the classical solid-state cells which are replaced by devices based on interpenetrating network junctions (Gratzel, 2004).

The use of dye molecules as light harvester in a solar cell (Dye-sensitized solar cell: DSSC) for future clean energy has been most attractive and successful when the dye is chemo-adsorbed on a porous network of interconnected nanometer-sized crystallites of a wide band gap semiconductor (O'Regan and Gratzel, 1991). The best studied example is the Ruthenium-bipyridyl dyes which shows a high conversion efficiency of about 11 to 12% (Mohammed et al., 2005; Nezeeruddin et al., 1993; Gao et al., 2000; Andre et al., 2004). However, these Ru-polypyridyl complexes contain heavy rare metal, which is undesirable from the environmental aspect point of view; besides, the process to synthesize the complexes is complicated and costly. Therefore, natural dyes can be adopted as alternative for the same purpose with an acceptable efficient metal-to-ligand charge transfer (Cherepy et al., 1997). The advantages of natural dyes include their readily availability, low cost and their simple extraction into cheap organic solvents which can be applied without further purification. In nature, both the different parts of the shoot and root systems of plant show various colours from red to purple, and contain various natural dye which can be extracted by simple laboratory procedures. Natural dye extracts containing anthocyanins (Calogero and Marco, 2008; Smestad, 1998)

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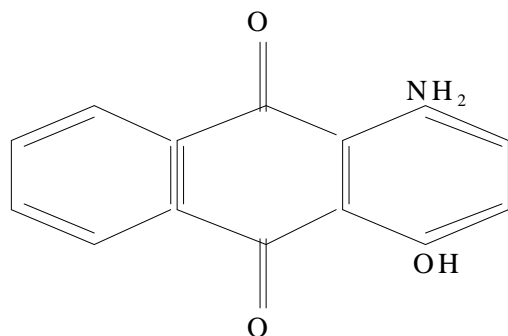


Figure 1. Structure of Duranol red from *A. cepa*.

and carotenoids (Fernando and Senadeera, 2008) have shown different sensitizing performances. The carbonyl and hydroxyl groups present in the anthocyanin molecule bound to the surface of the porous TiO₂ film, this makes electron transfer from the anthocyanin molecule to the conduction band of the TiO₂ effective (Aduloju et al., 2011). In this contribution, the efficiency and stability of DSSCs sensitized using natural dyes from *Allium cepa* were discussed.

EXPERIMENTAL

Materials

Transparent conductive oxide coated glass (TCO, 10 to 12 ohm/m², 1.00 × 1.00 cm²), Ti-Nanoxide D and surlyn polymer foil were purchased from SOLARONIX. Dinitroamine platinum (II) was procured from Johnson Matthey catalysts for Counter anode preparation, acetonitrile, sodium carbonate and sodium acetate combined in making electrolyte were purchased from ALDRICH. Dye extract was obtained from the natural product (*A. cepa*).

Preparations of natural dye sensitizers

Red leaves of *A. cepa* were dried in an airy but dark place in the laboratory for several days until their weight becomes invariant. They were then crushed into tiny bits and extracted into a mixture of ethanol-fluka, 96% (v/v) and water (4:1 by volume) keeping them overnight.

The residual part was removed by filtration and filtrate was: (A) used as prepared and (B) washed with hexane severally to remove oil droplets and chlorophyll that may be present. Both A and B were then hydrolysed with few drops of HCl so that the extracts becomes deep red in colour as the natural pH of 3.1 was adjusted to 1.0. Both resulting extracts were centrifuged to further remove any solid residue and were used directly as prepared for the construction of the DSSCs at room temperature. In this condition, only the extract B remain stable for many months at room temperature in ethanol/water solvent.

Preparation of electrolyte

The electrolyte solution for natural DSSCs was prepared by dissolving 2.075 g of potassium iodide (KI) and 0.19 g of I₂ in 25 ml of ethylene glycol/acetonitrile mixture (4:1 by volume).

Preparation of DSSCs

TiO₂ paste purchased from Solaronix (nanoxide-T, colloidal anatase particles size ~13 nm, ~120 m²/g) was coated by screen printing method on pre-cleaned fluorine doped tin-oxide (FTO) conducting glasses. Finally, the glass sheet was sintered at 450°C for 30 min and furnace-step cooled to room temperature to melt together the TiO₂ nanocrystals and to ensure its good mechanical cohesion on the glass surface.

The TiO₂ electrodes thickness was determined by Dekar profilometer to be 8.10 μm. The impregnation of the electrode was achieved by the immersion of the electrode (face-up) in the natural dye extracts for 4 to 6 h, this turned the TiO₂ thick-film from pale-white to fairly reddish colour. The impurities/excess dye was washed away with anhydrous ethanol, dried in moisture free air and was stored in a dark anhydrous condition.

DSSCs of 1 cm² active area were assembled by sandwiching a 60 μm thick (before melting) surlyn polymer foil as spacer between the photoanode and the platinum counter electrode (prepared by spraying method). Sealing was done by keeping the structure in a hot-press at 80°C for 11 to 15 s. The cell was impregnated with the liquid electrolyte via a pre-drilled hole on the counter-electrode. The hole was later covered to prevent the electrode from leaking.

Measurements of photoelectrochemical characteristics

UV-visible absorption measurements of the extracts were carried out with Avante UV-VIS spectrophotometer. Photoelectrochemical measurements of DSSCs were performed under a standard solar radiation of 1000 W/m² using overhead Veeco-viewpoint solar simulator (equipped with AM 1.5 filter) and a four point Keithley multimeter coupled with a Lab-tracer software was used for data acquisition at room temperature. The active/working cell area was 1.00 cm².

Based on the I-V curve, power conversion efficiency (η) was calculated according to the equation:

$$\eta = FF \times J_{sc} \times V_{oc} / I \quad (1)$$

where J_{sc} is the short-circuit current (mA/cm²), I is the intensity of the incident light (W/m²), V_{oc} is the open circuit voltage (volts), FF is the fill factor defined as:

$$FF = J_m V_m / J_{sc} V_{oc} \quad (2)$$

where J_m and V_m are the optimum photocurrent and voltage that can be extracted from the maximum power point of the I-V characteristics (O'Regan and Graetzel, 1991).

RESULTS AND DISCUSSION

Figure 1 shows the UV-VIS absorption spectral of extracts A and B. Both dye extracts were soluble in ethanol/water solvent and resulted in deep coloured solutions. It can be seen that the extract A exhibits a maximum at 532 and 450 nm, while B at 532 nm shows an absorption maximum (Figure 2). The B-band is broadened with a shoulder at 490 nm. The difference in the absorption characteristics is due to the different composition of chlorophyll (450 nm) and Duranol (532 nm) in the solutions which in turn gives different colours to the extracts. Table 1 shows the maximum reproducible values of the energy conversion efficiency, the open-

Table 1. Photoelectrochemical parameters of the DSSCs sensitized by natural dyes A and B under irradiation with simulated sunlight at 1000 W/m² intensity (AM 1.5) at the working area of 1.0 cm².

DSSC sensitizer	J _{sc} (mAcm ⁻²)	V _{oc} (mV)	FF	η (%)
Extract A	0.85	0.65	0.53	0.29
Extract B	0.67	0.58	0.68	0.26

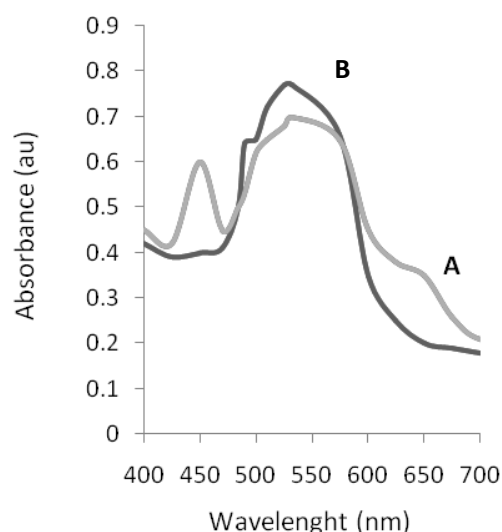


Figure 2. Absorption spectra of (A) Duranol and chlorophyll and (B) Duranol from *A. cepa*.

circuit voltage and the short-circuit photocurrent of the cells sensitized with extracts A and B.

The energy conversion efficiency of the cell sensitized with extract A is significantly higher than B cell, this could be attributed to the fact that cell made from extract A enjoys sensitization at peaks 532 and 490 nm, respectively (as depicted in Figure 1). However, no deviation from this trend was observed when attempts were made to enhance the absorption of the individual dyes (that is, by varying the duration of immersion). However, both cells show no invariance in the efficiency under 3 h continuous stimulated sunlight illumination, but on exposure to direct sunlight noticeable decay was seen in about 4 to 5 h in both cells. This effect could be attributed to the UV in sunlight which seems to degrade the pigments as observed in the fairly fading away of the photoanode colour.

Conclusion

In this approach, natural dyes were extracted from *A. cepa* using different cheap techniques for possible application as sensitizers in DSSCs. The attached dyes, rather than the semiconductor itself, are the absorbing

species. They inject electrons into the semiconductor conduction band upon excitation. These electrons are then collected at a conducting surface, generating photocurrent. As a result of this advancement, the development of low-cost, efficient photochemical solar cells became possible.

Among the different dyes investigated, the dye containing mixture of chlorophyll and Duranol extracts gave a significantly higher photocurrent, voltage and reasonable efficiency; this could be due to better interaction between the surface of TiO₂ and the dye molecules. However, studies on the long-term stability of the cell developed revealed decay in the efficiency over time.

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