Optical Materials 52 (2016) 150–156

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Dye-sensitized solar cell using extract from petals of male flowers *Luffa cylindrica* L. as a natural sensitizer

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ARTICLE INFO

Article history:
Received 3 October 2015
Received in revised form 8 December 2015
Accepted 11 December 2015
Available online 29 December 2015

Keywords:
Dye-sensitized solar cell
Natural dyes
TiO_2 film
Energy conversion

ABSTRACT

The study reports use of natural dye extracted from petals of male flowers *Luffa cylindrica* L. as sensitizer for TiO_2 based dye-sensitized solar cells. Optical characteristics of the dye extract and photoelectrochemical performance of the cells were studied. The extracts showed the UV–Vis absorptions in the 400–450 nm range with broad maxima at ~430 nm. FTIR spectra of extract revealed the presence of anchoring groups and coloring constituents. DSSC was fabricated using natural dye loaded TiO_2 photoelectrode, electrolyte containing I^-/I_3^- redox mediator and Pt counter electrode by assembling them into a cell module. Conversion of solar light into electricity was successfully accomplished and DSSC based on petals of male flowers *Luffa cylindrica* L. extract exhibited an open-circuit voltage (V_{oc}) of 0.52 V, short-circuit current density (J_{sc}) of 0.44 mA cm^{-2}, P_{max} 130 μW, fill factor (FF) of 0.60, conversion efficiency of 0.13% and IPCE ~30% (at $\lambda = 430$ nm).

1. Introduction

Dye-sensitized solar cells (DSSC) are energy devices that convert light energy into electricity, based on the sensitization of wide-band gap metal oxide semiconductors such as TiO_2 [1,2]. Successfully demonstrated by O'Regan and Gratzel in 1991 [1], the DSSC devices have attracted a lot of interest towards development and improvement of new families of dyes [3]. DSSCs sensitized with dyes having heavy transition-metal complexes such as ruthenium based complexes are the most efficient and have been recorded to operate with power conversions efficiency reaching as high as 11–12% using nanoporous TiO_2 electrodes [4–6]. However, ruthenium polypyridyl complexes contain a heavy metal, which is undesirable from environmental concerns [7]. Additionally, the high cost of ruthenium complexes and the long-term unavailability of these noble metals [4–9] switch the need to search for alternative photosensitizers to be used for TiO_2-based photovoltaic devices. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency [7,10–16].

Recently, research has focused on the easily available dyes extracted from natural sources as a photosensitizer because of their large absorption coefficients, high light-harvesting efficiency, low cost, easy preparation and environment friendliness [17–25]. Natural pigments containing anthocyanins [12,16,26–29] and carotenoids [30] have shown overall solar energy conversion efficiencies below 1%. The pigments are present in the different part of the plant including flowers petals, fruits, leaves, stems and roots. The anthocyanins belong to the group of natural dyes responsible for several colors in the red–blue range, found in fruits, flowers and leaves of plants. Carbonyl and hydroxyl groups present in the anthocyanin molecule can be bounded to the surface of a porous TiO_2 film. This makes electron transfer from the anthocyanin molecule to the conduction band of TiO_2 feasible [13].

In this work, a common group of natural dyes abundant in flowers, namely Flavonoids, is tested for its performance in DSSC. Flavonoids are sugar bound polyphenols found in all land plants. A class of flavonoids called anthocyanins is responsible for the red and purple coloration of many fruits and flowers. Flavonoids are the most important plant pigments for flower coloration, producing yellow or red/blue pigmentation in petals designed to attract pollinator animals. Basic structures of Flavonoid, Flavone and Anthocyanin are shown in Fig. 1(a).The natural dyes used in this work, were obtained from petals of male flowers of *Luffa cylindrical* L. which are identified to be rich in luteotin-7-glucoside and chrysoriol-7-glucoside shown in Fig. 1(b) and (c) [31,32].

Optical characteristics of the dye extract were studied by FT-IR and UV–Vis absorption spectroscopy. AFM images were taken to observe the morphological changes. The cyclic voltammetry (CV) and UV–vis absorption data were used to ascertain the compatibility of energy positions and feasibility of transitions. DSSC using

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http://dx.doi.org/10.1016/j.optmat.2015.12.016
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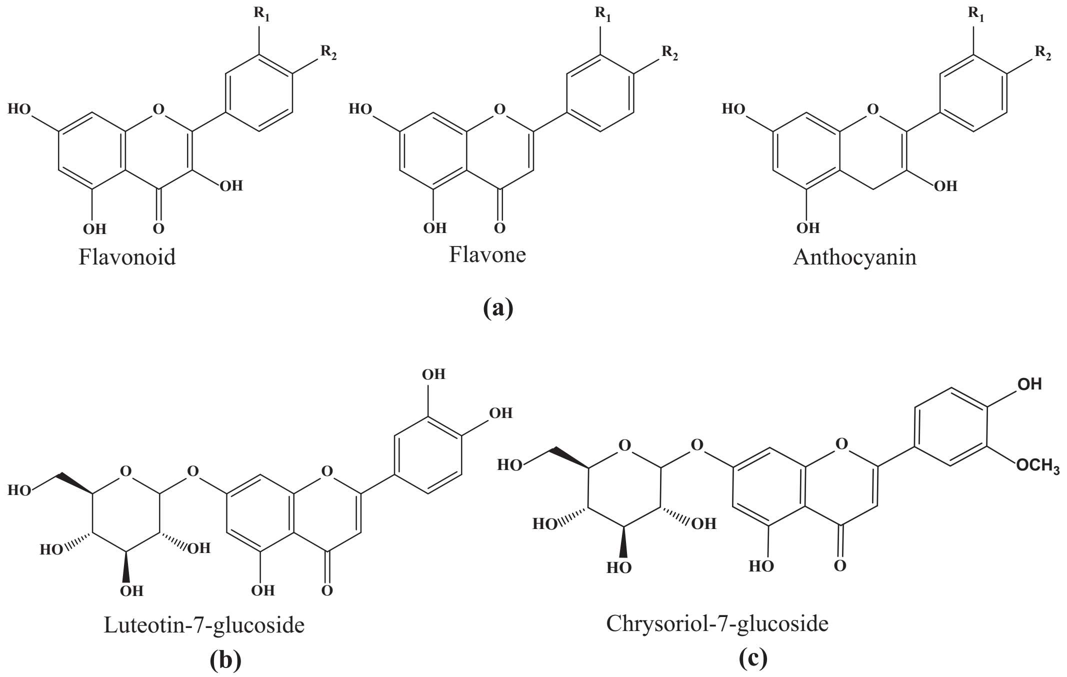

Fig. 1. Structures of (a) Flavonoid, Flavone and Anthocyanin, (b) luteotin-7-glucoside and (c) chrysoriol-7-glucoside.

natural dye extract from petals of male flowers of *L. cylindrical* L. coated TiO_2 were fabricated and photoelectrochemical performances of the cell were investigated.

2. Materials and methods

2.1. Materials

All the chemicals were of reagent grade and purchased from commercial sources and used without further purification. Ethanol (A.R. grade, 99.9%, Merck, India) was used for extracting natural dyes from plants. Acetonitrile used as solvent was procured from Merck, India. Titanium paste (HT), platinum catalyst (T/SP) and the sealing tape (SX1170-60, 50 μm thick) were obtained from Solaronix. Anhydrous lithium iodide (99.9%, Aldrich) and iodine (G. R. grade, 99.8%, BDH) were used as redox couple in photo-electrochemical (PEC) experiments without any further purification. FTO (Fluorine-doped tin oxide) coated conductive glass slides (surface resistivity 10 Ω/□, thickness 2.2 mm) obtained from Solaronix Switzerland, were used as substrates for preparing TiO_2 thin film electrode and Platinum counter electrode. Tetrabutyl ammonium perchlorate used as supporting electrolyte was obtained from Fluka.

2.2. Apparatus and instruments

A bipotentiostat (AFRDE 4E, Pine, USA), along with an ecorder (Model 201, eDAQ, Australia), was used for all current–potential measurements. Cyclic voltammograms of the natural dyes were recorded using acetonitrile solution of the test dyes and 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte. Ag/Ag^+ (in acetonitrile) was used as reference electrode and platinum wire as working electrode.

For photoelectrochemical (PEC) measurements, a 150 W Xenon arc lamp with lamp housing (Model No. 66057) and power supply (Model No. 68752), all from Oriel Corporation, USA, was used as the light source and the semiconductor electrode was illuminated after passing the light beam through a 6 in. long water column (to filter IR) and condensing it with the help of fused silica lenses (Oriel Corporation, USA). For selective excitation of dye only (not TiO_2), the UV part of this IR-filtered light was cut off by using a long pass filter (Model No. 51280, Oriel Corporation, USA) and the light obtained this way is mentioned as "visible light. The monochromatic light, when required, was obtained by using a grating monochromator (Oriel Model 77250 equipped with Model 7798 grating). The width of the exit slit of the monochromator was kept at 0.5 mm. To obtain the action spectrum (J_{photo}–λ) of the dye-sensitized TiO_2 electrode, monochromatic light-induced photocurrent was measured with a digital multimeter (Philips Model No. 2525). The absorption spectrums were recorded by Shimadzu UV-1700 spectrophotometer. The FTIR spectra were recorded by Varian 3100 FT-IR spectrometer. AFM images were recorded by NT-MDT atomic force microscope (model Solver NEXT). Roughness of the surface was reckoned by NOVA Px 3.1.0 software.

2.3. Preparation of natural dye sensitizers

Fresh petals of male flowers *Luffa cylyndrica* L. were washed with deionized water and vacuum dried at 60 °C. The dried petals of male flowers *L. cylyndrica* L. were crushed into fine powder; 1 g of the powder was immersed in 50 mL ethanol and kept for 24 h. Subsequently solid residue was filtered out and the resulting dye solution was used as sensitizer. The extracts were properly sealed, protected from direct sunlight and used further as dye sensitizer.

2.4. Preparation of TiO_2 photoanode and platinum counter electrode

TiO_2 thin film electrode (photoanode) was prepared from highly transparent TiO_2 paste spread on FTO-coated conductive glass plate by the doctors' blade method. FTO was cleaned by successive immersions in acetone; ethanol and deionized (DI) water for approximately 10 min each, in an ultrasonic cleaner before cell fabrication. On the conducting side of glass substrate, a U-shaped frame of adhesive tape was applied to control the thickness of the film and to provide non-coated area for electrical contact. After spreading TiO_2 paste, the adhesive tapes were carefully removed