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Sensitization of Photoelectrochemical Solar Cells with a Natural Dye Extracted from *Kopsia flavida* Fruit

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ABSTRACT

The use of natural dyes in solar cells offers promising prospects for the advancement of this technology, because bringing down the manufacturing cost of solar cells is a scientific challenge. The use of synthetic organic and metalorganic dyes involve several problems, such as long procedures of chemical synthesis, poor yield and high cost of rare metals etc. Therefore investigation on various natural pigments found interesting. In this paper, we report on the fabrication of dye sensitized solar cell functionalized with a natural dye extracted from the bark of the *Kopsia flavida* fruit that contain functional groups such as OH, which is suppose to be an anthocyanin dye. Cell shows photocurrent more than 1.2 mA/cm^2, photovoltage of 520 mV and fill factor nearly 62%.

1. INTRODUCTION

Dye-sensitized solar cells (DSC) based on TiO_2 nano-particles were first developed by Grätzel and coworkers more than two decades ago. These regenerative photoelectrochemical cells composed of nano-porous TiO_2 films sensitized with a dye. When the cells are illuminated with visible light dye adsorbed on TiO_2 film injects electrons into the conduction band of the semiconductor. Then the charge carriers diffuse to the conducting tin oxide (CTO) glass substrate on which the TiO_2 film is coated and pass through the external circuit generating a photocurrent. The photo excited dye is reduced by accepting an electron from the redox couple in the electrolyte, which is regenerated again acquiring an electron at the counter electrode.

The use of natural dyes in solar cells offers promising prospects for the advancement of this technology, because fabrication of cost effective solar cells is a scientific challenge. The use of natural pigments cut down the cost of chemical synthesis and high cost of rare metals need for metal organic dye sensitizers. Therefore lot of interest has been drawn on natural dyes which extracted from plant materials. Several natural pigments have been utilized as sensitizers in photovoltaic cells due to their capability of injecting electron from excited pigments to the conduction band of the semiconductor material. Most natural pigments that can be utilized in dye sensitized solar cells undergo rapid photo degradation. Cyanidin is an organic dye of the flavonoid class found in leaves and fruits of plants and responsible for the colours of various vegetable tissues, which have been studied as a sensitizer in solar cells that found to be photo stable.

In this paper, we report on the fabrication of dye sensitized solar cell functionalized with a natural dye which was extracted from bark of the fruit of *Kopsia flavida*, which contain anthocynine dye with the functional groups capable to attach on oxide semiconductor films.

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2. EXPERIMENTAL

2.1 Preparation of TiO_2 films

TiO_2 films on CTO glass were prepared as follows. 1 g of Degussa (p-25) powder was weighted and 2 ml of acetic acid was added to this powder in an agate mortar. Then it was ground well with the addition of 2 ml of ethanol. This paste was used to coat a film on the CTO glass using the doctor blade method. The films were sintered at 450 °C in a furnace for 30 minutes after drying them at 120 °C on a hot plate.

2.2 Extraction of dye

The bark of the fruit was carefully peeled off and put into a beaker. Then 99.9% ethanol was added to the beaker and it was kept in a water bath maintained at about 70 ^{0}C for four hours. The solid residues were filtered out to obtain a clear dye solution. After that purple colour dye extraction was transferred to a test tube and kept close until use.

2.3 Process of dye coating and cell assembly

The dye was coated on TiO_2 films by immersing the film for 12 hours in the dye solution extracted from the fruits of *Kopsia flavida* into ethanol. The photoelectrochemical solar cells were made by placing the dye coated TiO_2 plate on CTO glass and filling the capillaries of the mesoporous film with an electrolyte containing 0.5 M tetrapropyl ammonium iodide and 0.05 M iodine in mixture of acetonitrile and ethylene carbonate in 1:4 ratio by volume.

2.4 Characterization of the dye and the solar cells

The absorption spectra of the dye in the ultraviolet and visible region were recorded using a HP 8452A diode array spectrophotometer. I–V characteristics of the cells at 1000 Wm^{-2} and 1.5 AM simulated sunlight were recorded using a Keithley source meter. A Xe lamp was used as the solar simulator calibrated with a silicon photo diode to set the light intensity at 1000 W m^{-2}. For the IR measurements, dye solution was heated until the ethanol is evaporated and powder of the dye was collected. 1 cm diameter and constant-weight KBr pellets were prepared by mixing fused-KBr and dye sample in 20:1 ratio and the spectra were measured in 400-4000 cm^{-1} region for transmission mode. The spectra were analyzed by applying the method of curve decomposition using fitting software built-in with the FTIR spectrometer (NICOLET 6700).

3. RESULTS AND DISCUSSION

The dye extracted from the bark of the *Kopsia flavida* fruits in ethanol solution exhibited absorption peak at around 550 nm in visible region (Fig. 1). It also strongly absorbs light in the ultraviolet region functionalizing as a UV filter. UV light falls on high band gap semiconductors generate electron and hole pairs on which the dye is

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adsorbed. The electron and hole pairs generate in high band gap semiconductor materials leads to photo degradation processes in dye sensitized solar cells and it was reported that UV filters improve the lifetime of the solar cells. Therefore this pigment appears itself as a UV filter protecting the solar cell.

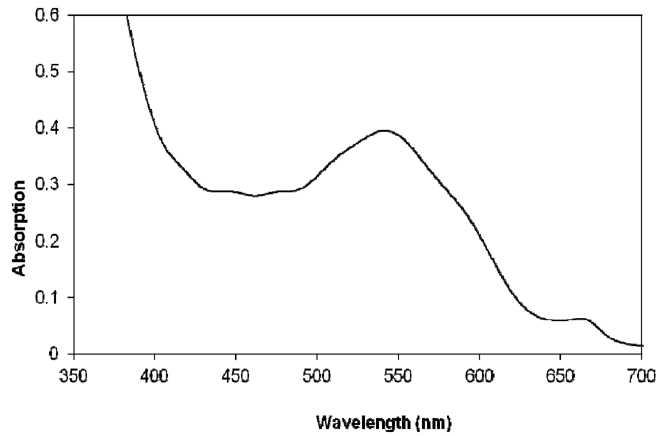

Fig. 1: UV visible spectra of dye extracted from the bark of the *Kopsia flavida* fruit

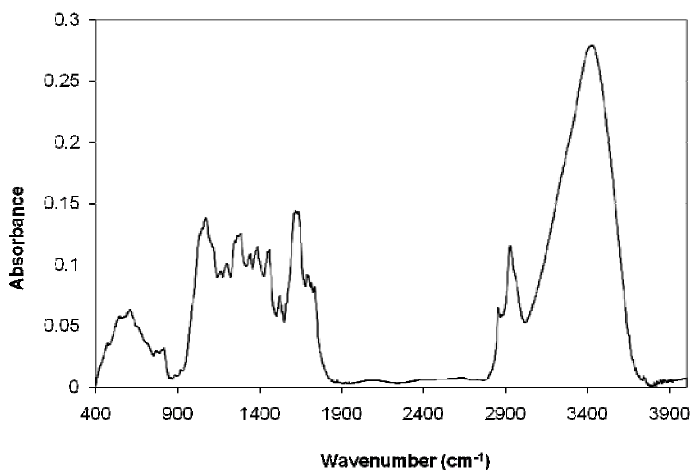

Fig. 2: FTIR spectra of dye extracted from the bark of the *Kopsia flavida* fruit

FTIR data (Fig. 2) convinces that the dye contains hydroxyl groups which help the dye to attach effectively on TiO_2 film by eliminating water molecules. The broad band at around 3400 cm^{-1} suggests that the dye molecule accompany with a glucoside. Previous studies report that the anthocyanin dyes with gucosides improves the photocurrent of dye sensitized solar cells [6]. Therefore possible structure for the cyanine dye extracted from the bark of the *Kopsia flavida* fruit is likely to be shown in Fig. 3 that has to be confirmed with NMR data.

Cyclic voltogram of pigment extracted from *Kopsia flavida* fruit coated on TiO_2 film is shown in Fig. 4. When the electrode potential is negatively swept, peak appears at

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-1.5 V versus SCE. This oxidation potential is well above the energy (-0.5 eV) of the conduction band of TiO_2. Therefore electron injection to the semiconductor from the excited dye molecule is feasible generating a photocurrent in the DSC.

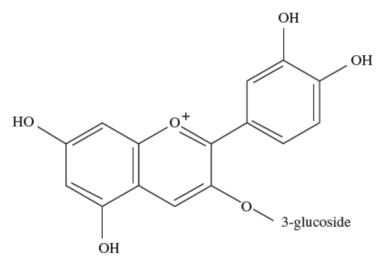

Fig. 3: Possible structure of the dye in extraction of *Kopsia flavida* fruits

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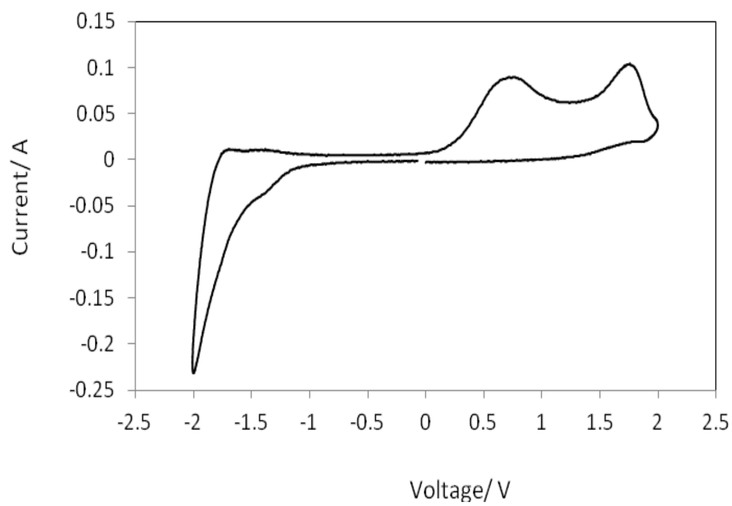

Fig. 4: Cyclic voltogram of pigment extracted from *Kopsia flavida* fruit

The I-V curve in figure 5 for the DSC sensitized with the dye extracted from *Kopsia flavida* fruits shows photocurrent more than 1.2 mA/cm^2. The reported photocurrents for the DSCs with natural pigments are generally lower than synthetic dyes because other pigments in the dye extraction such as tannins and carboxylic acids that do not produce any photocurrent absorbing visible light also co-adsorbed with the active pigment. These co-adsorbants shifts the quasi Fermi level of TiO_2 making photo injection of electrons from the active pigment difficult. But at the same time photo voltage and fill factor of the cell improves by the co-adsorbants. Since we have used the extraction of *Kopsia flavida* fruits without any purification high photovoltage of 520 mV and fill factor of 62% of the cell compared to purified cyanidin dye gives evident for this scenario. Therefore it is promising that this natural pigment will deliver a higher photocurrent after purification of the extraction to obtain the active pigment.

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Fig. 5: I-V curve with dye extraction in *Kopsia flavida* fruit

4. CONCLUSION

The dye which was extracted from *Kopsia flavida* fruit has comparably higher photocurrent, photovoltage, efficiency and fill factor as other natural pigments that have been previously reported. The active pigment seems to have a potential as a sensitizer of DSCs after its isolation and purification.

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