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Natural Dye Extracted from *Rhododendron* Species Flowers as a Photosensitizer in Dye Sensitized Solar Cell

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The natural dye, anthocyanin, was extracted from the flowers of *Rhododendron* species with three different colors, pink, red and violet, using a simple extraction technique, and was used as the sensitizer in dye-sensitized solar cells. The dyes were treated with nitric and acetic acids to examine their effects on the power conversion efficiency. According to the experimental results, the performance was better with the acetic acid-treated anthocyanin. The Jsc value for the acetic acid-treated pink, red and violet dyes increased to 0.887, 0.932 and 0.737 mA/cm^2 compared to nitric acid treated and bare dye. The conversion efficiency of the acetic acid-treated pink, red and violet was 0.35%, 0.36%, 0.28%, respectively, which was higher than the nitric acid-treated and bare dye. This paper briefly discusses the simple extraction technique of these natural dyes and their performance in DSSCs.

Keywords: Natural dye, Anthocyanin, FT-IR, Conversion efficiency

1. INTRODUCTION

The dye-sensitized solar cell (DSSC) is a device used to convert light energy to electrical energy, and is based on the sensitization of wide band gap semiconductors using dye molecules [1]. DSSCs have attracted considerably more attention in recent years because of their promising solar energy conversion systems. In the assembly of DSSC, the dye plays an important role in harvesting solar energy and converting it to electrical energy with the aid of a semiconducting photoanode.

Therefore, the cell performance is totally dependent on the type of dye used as a sensitizer. Many metal complexes and organic dyes have been synthesized and used as sensitizers. Ruthenium (Ru) complexes are considered good sensitizers for DSSCs because of their intense charge-transfer absorption over the entire visible range and highly efficient metal-to-ligand charge transfer [2]. The major drawback of Ru is its rarity, high cost and the complicated synthesis of ruthenium complexes.

Accordingly, alternative, readily available and efficient photosensitizers at low cost is a scientific challenge for TiO_2-based photovoltaic devices. Recently, research has focused on the easily available dyes extracted from natural sources and as a photosensitizer because of its large absorption coefficients, high light-harvesting efficiency, low cost, easy preparation and environment friendliness. Thus far, several dyes extracted from natural sources, such as black rice, capsicum, *Erythrina variegata* flower, *Rosa xanthina* [2], curcumin, red-perilla [3], rosella flower, blue pea flower [1], *Jathropha curcas*, *Citrus aurantium* [4], red cabbage [5] etc., have been used as sensitizers in DSSC because the application of naturally available pigments, such as anthocyanins, carotenoids and cholorophylls, for DSSCs has several advantages over rare metal complexes. In this context, anthocyanin is one such flavanoid compound present in many fruits, flowers and leaves, and is responsible for the red, violet and blue colors [6-8]. The advantage of anthocyanin (Fig. 1) is the binding of carbonyl and hydroxyl groups to the surface of a porous TiO_2 film. This causes electron transfer from the anthocyanin molecule to the conduction band of TiO_2 [9].

In this study, DSSCs were assembled using natural dyes extracted from three different colored flowers of *Rhododendron* species using a very simple extraction technique. Because the performance of the raw dye is better than the commercial or purified analogues, the dye was extracted using a minimal chemical procedure without further purification because the presence of a natural extract like alcohols, organic acids, etc. act as coadsorbates, suppressing recombination with the electrolyte, reducing the level of dye aggregation and favoring charge injection [10]. The extracted dyes were characterized by Fourier transform infrared (FT-IR) and UV–vis absorption spectroscopy. The photoelectrochemical properties of the pure and acidified extracts, which were used as sensitizers in DSSCs, were examined.

2. EXPERIMENTAL DETAILS

2.1 Preparation of dye sensitizer solutions

The flowers of the *Rhododendron* species with three different colors (pink, red and violet) were collected fresh in South Korea and placed in a vacuum furnace for ~ 10 h at 65° C to remove moisture. After drying, the flowers were crushed in a mortar and pestle and prepared as a powder. Approximately 1g of the powdered sample was dissolved in 60mL of ethanol and kept overnight at ambient temperature for adequate extraction without exposure to sunlight. After extraction, the solid residues were filtered and the clear dye solutions were used as a sensitizer. The dye solution was also characterized by UV-Vis absorption. For FT-IR, the residue of the dye solution was collected by evaporating the ethanol on a hot plate. The freshly prepared extracts were then treated with nitric

(0.01N, pH 1) and acetic acid (0.4N, pH 4), and used as a sensitizer in solar cells to evaluate the photoelectrochemical performance.

2.2 Solar cell assembly

A fluorine-doped Tin Oxide glass plate with resistance of 13 Ω/sq was first cleaned with acetone, ethanol and water for approximately 10 minutes each using an ultrasonic bath. Scotch tape was used as a spacer to control the film thickness and provide non-coated areas for electrical contact. For the photoanode, a TiO_2 (Ti-Nanooxide T/SP, Solaronix) paste was coated on a FTO plate using the doctor blade method. The coated TiO_2 films were then air-dried for ~ 5 min to reduce the surface irregularities. The films were annealed at 550°C in air for 30 minutes to remove the organic loads and facilitate the interconnection of TiO_2 nanoparticles. The film thickness was ~ 20 µm. The active area of the TiO_2 electrodes was 0.27 cm^2. After cooling at 75°C, the TiO_2 film electrodes were immersed in an anthocyanin dye solution for 24 hrs. After dye adsorption, the film was rinsed with pure ethanol and dried with hot air. A Pt electrode was prepared from Pt paste (platisol T/SP, Solaronix) using the doctor blade method. After coating on a FTO plate, it was heated at 450°C for 30 min. The dye-covered TiO_2 photoanode and Pt counter electrode were assembled as a sandwich-type cell using a thermoplastic hot-melt ionomer film (SX 1170, Solaronix). A drop of an Iodolyte AN-50 electrolyte solution was injected into the cell through a hole at the back of the counter electrode. The hole was covered with a cover glass on a hot-melt ionomer film and then sealed. Finally, to achieve good electrical contact for the measurements, the edge of each side of the FTO glass was cleaned and soldered (ultrasonic soldering system, Model-9200) with alloy #143 (Cerasolza).

2.3 Characterization of TiO_2 powder

The structural characterization of the extracted anthocyanin pigment was characterized by FT-IR spectroscopy (Nicolet-380 spectrometer) using KBr pellets. UV-Vis spectroscopy was performed using an Optizen 3220UV. The current density-voltage (J-V) measurements were carried out under one sun illumination (AM1.5G) using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp) with an intensity of 100 $mWcm^{-2}$. A Keithley 2400 was used as the source measurement unit. The photoelectric conversion efficiency (η) was calculated using the following equation:

$$\eta(\%) = \frac{V_{OC} \times I_{SC} \times FF}{P_{in}} \times 100$$

where η is the global efficiency, and V_{OC}, I_{SC} and FF are the open-circuit voltage, short circuit current density and fill factor, respectively. P_{in} is the maximum input of light energy.

3. RESULTS AND DISCUSSION

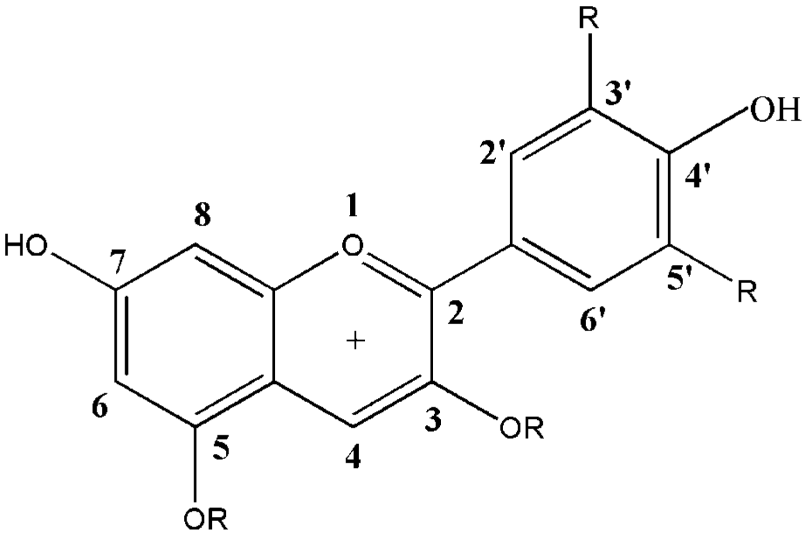

Figure 1. Anthocyanin flavylium chromophore, a carboxonium cation: R= sugar or acylated sugar

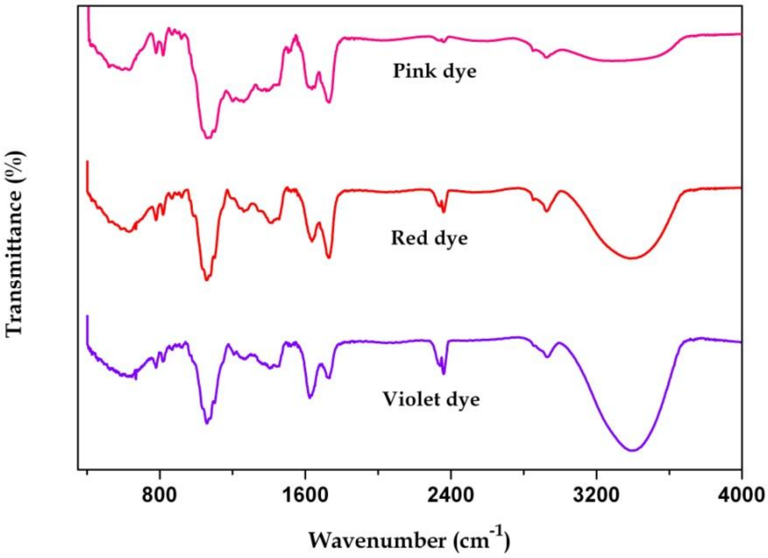

Figure 2. FT-IR spectra of the anthocyanin pigment extracted from the three different colored flowers of *Rhododendron* species

3.1 FTIR Spectra

The anthocyanin pigment extracted from the *Rhododendron* flowers using ethanol was confirmed by FTIR spectroscopy. The FTIR spectra were similar to the spectra reported by Luo *et al* [11]. Fig. 2 shows the FT-IR spectra of the anthocyanin pigment of three different colors. All three different colored dyes have a similar spectral structure. The two peaks at 2922 and 2850 cm^{-1} were assigned to the –CH stretching modes. The peak at a wavenumber of 3393 cm^{-1} corresponds to the OH stretching vibration. The spectral region between 1550 to 1700 cm^{-1} allows infrared absorption of

C=C. Consequently, the peak at 1630 cm^{-1} corresponding to the double bond (C=C) stretching vibration and can be correlated with the stretching of aromatic C=C in anthocyanin. The peaks at $1726 cm^{-1}$ were assigned to the C=O stretching vibration for all three colors [11,12]. This suggests that the anthocyanin in the dye has a partial quinonoidal form. On the other hand, the intensity of the peak at $1726 cm^{-1}$ was high with the pink and red dyes compared to the violet dyes. All the stretching vibrational modes coincided with the four isolated anthocyanin pigments extracted from *canna indica* flower [13]. This confirmed the presence of anthocyanin pigments in the extract of *Rhododendron* flowers.

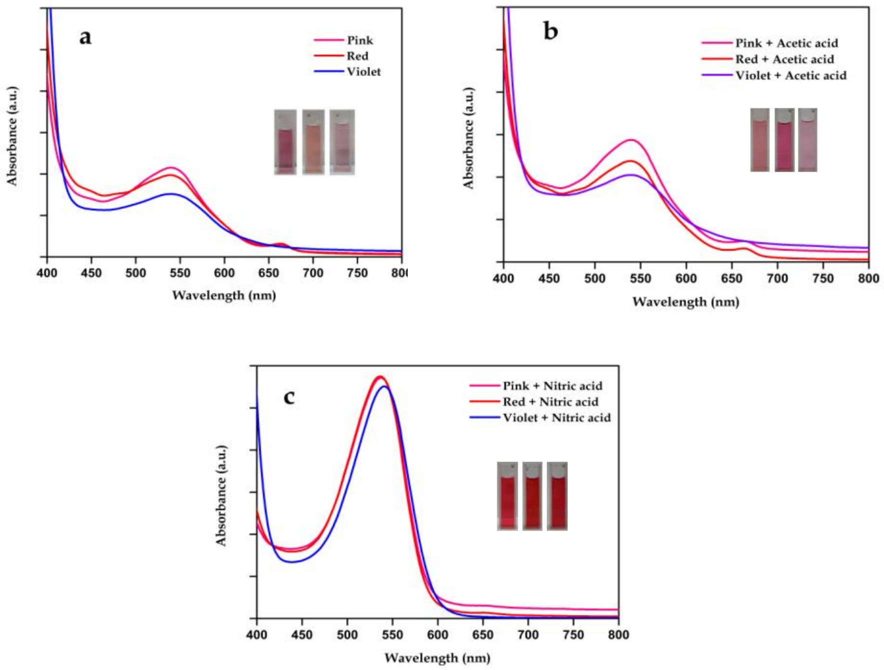

Figure 3. UV-Vis absorption spectra of the *Rhododendron* extract (a) fresh dye solution, (b) acetic acid treated dye solution, (c) nitric acid treated dye solution. The inserted optical photos show the three different colors of the dye solution (from left pink, red and violet).

3.2 UV-Vis absorption spectra

Fig. 3a and 4a shows the UV-Vis absorption spectra of the fresh dye solution extracted from *Rhododendron* species with three different colors (pink, red and violet), and after the dye was adsorbed on TiO_2, respectively. A sharp absorption spectrum was obtained for the pink, red and violet dyes at ~ 540 nm but the intensity of the absorption varied; it was higher with the pink and red dyes than with violet. After immersing the TiO_2-coated photoanode in the red and pink dye extract, the TiO_2 films turned a red and pink color, but turned a light violet for the violet colored dye (see the inset fig.4a). Fig. 4a shows the dye adsorbed on the TiO_2 with an absorption maximum at 540 nm. The absorption band of the adsorbed dye was broader than the absorption band of the fresh dye solution (Fig.3a) and the tail absorption extended up to 700 nm.

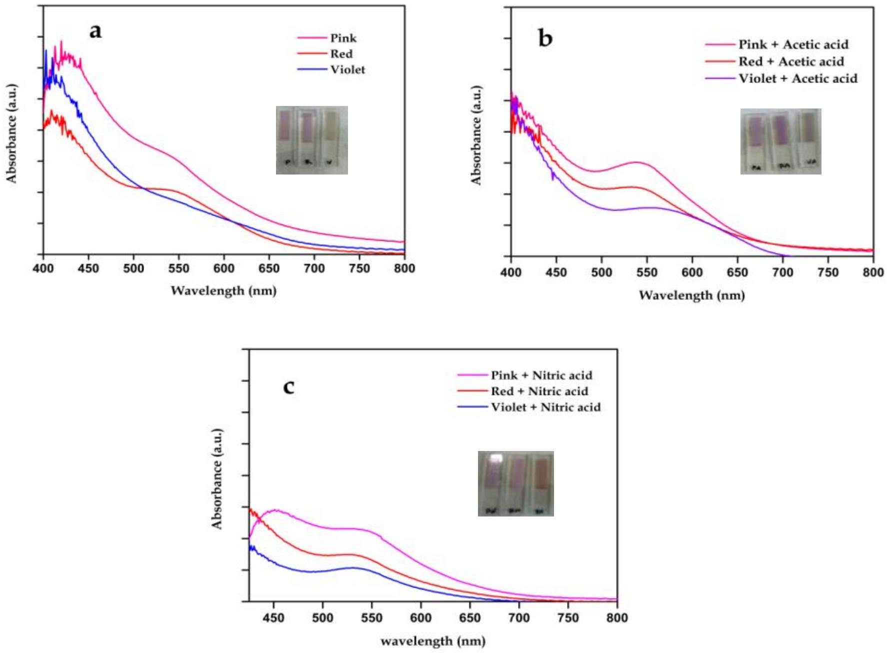

Figure 4. UV-Vis absorption spectra of the dye adsorbed on TiO_2 photoanode (a) fresh dye solution, (b) acetic acid treated dye solution, (c) nitric acid treated dye solution. The inserted optical photos show the three different colors of the dye adsorbed on TiO_2.

This broad absorption band was attributed to the binding of the anthocyanin molecule to the oxide surface of the photoanode [11].

The color of the dye turned dark after the acid treatment because the dye was pH dependant and solvent sensitive [14]. Fig. 1 shows the structure of the positively charged flavylium cation, which is the dominant equilibrium form under acidic conditions. The positive charge was delocalized through the pyrylium moiety, but carbons 2 and 4 were more positively charged atoms. The easy deprotonation of the two OH groups at positions 4’ and 7 contributes to the color changes in anthocyanin [15].

According to the literature, the absorption band of the anthocyanin pigment is pH sensitive so the extracted anthocyanin pigment was acidified with nitric and acetic acids and the absorption intensity was observed for the acidified dye solution and pure dye solution. The absorbance was high in the same order, i.e. pink, red and violet, for both the pure dye and acidified dye solutions (Fig. 3a,b,c). The absorbance intensity of the nitric acid-treated dye were very high compared to the acetic acid treated dye (Fig. 3b,c), because nitric acid is a strong oxidatic acid, whereas the acetic acid is a weak acid. In the case of an untreated fresh dye solution, the intensity was quite low compared to the acid treated dyes. On the other hand, the spectra of all the dye-adsorbed TiO_2 films were broadened and less intense compared to the corresponding dye solutions, and the tail of the absorption extended up to 700 nm in the bare and acid-treated TiO_2 films (Fig. 4a,b,c). The broadening and lower intensity is due to the adsorption of anthocyanin to the semiconductor TiO_2 surface. This chemical adsorption occurs because of the binding of alcoholic-bound protons with the hydroxyl group in the surface of nanostructured TiO_2. This confirmed the adsorption of dye molecules on the TiO_2 surface. These effects were observed for anthocyanins upon complexation with Ti metal ions [16]. Although the absorbance band was broadened for acetic acid and nitric acid-treated TiO_2 adsorbed dye, the intensity of dye adsorption was similar for the bare dye and acetic acid-treated dye, but the intensity was low for the nitric acid-treated dye. This might be due to etching of the TiO_2 surface by nitric acid. In contrast, the acidic acid-treated dye adsorbed photoanode was not affected because acetic acid is a weak acid. The bare and acidified dye adsorbed TiO_2 showed similar UV absorption spectra.

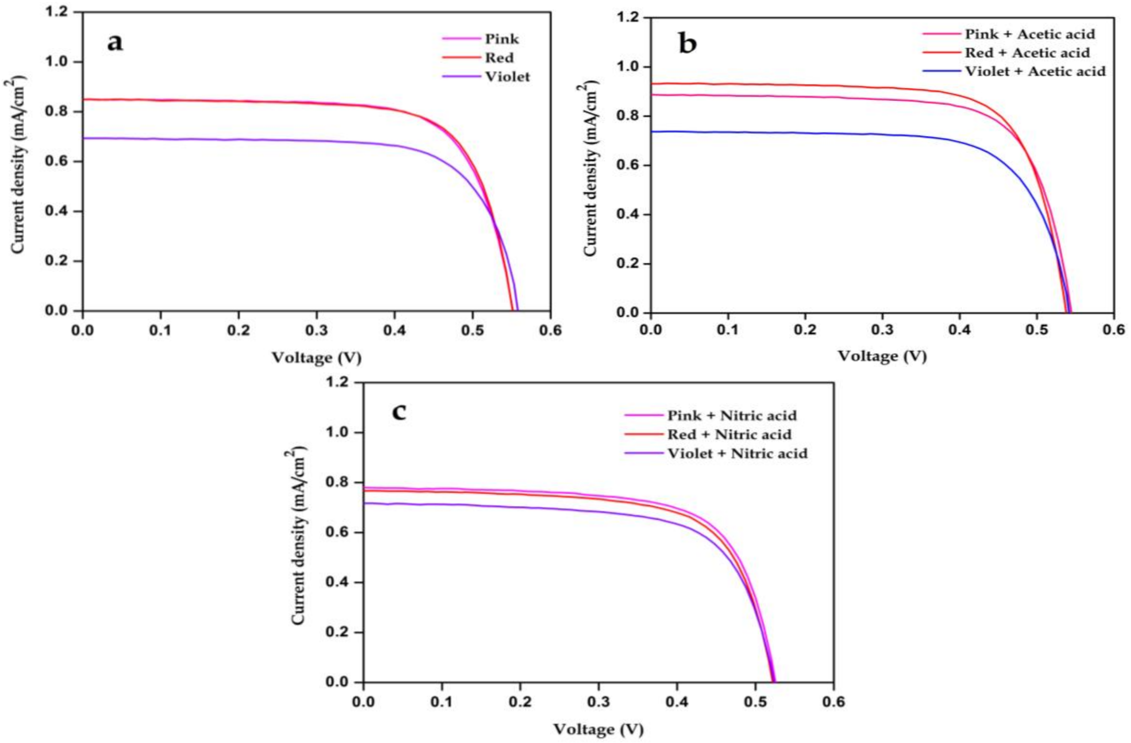

Figure 5. Current-voltage (I-V) characteristics of the photovoltaic devices sensitized with (a) pink, red, violet color dye (b) acetic acid treated dye (c) nitric acid treated dye.

3.3 Influence of different types of acid-treated anthocyanin pigment on photoelectrochemical performance

The photoelectric performance of the DSSCs is related to acidified and unacidified anthocyanin pigment. Table 1 lists the comparative performance of three different color dyes treated with nitric and acetic acid and the untreated dye in terms of the short circuit photocurrent (Jsc), open circuit voltage (Voc), fill factor (FF) and energy conversion efficiency (η). Fig. 5 shows the I-V curve of the bare dye and dye treated with nitric and acetic acid. The open-circuit voltage (Voc) of the bare pink, red and violet dye was 0.5516, 0.5439 and 0.5439 V, respectively. The short-circuit current density (J_{SC}) was 0.8492, 0.8503 and 0.6938 mA/cm^2, and fill factor (FF) was 0.7201, 0.7231 and 0.7159 and conversion efficiency was 0.33%, 0.33% and 0.27%, respectively. The performance of natural dye was lower than the N719 dye due mainly to the molecular structure of natural dye. The natural dye mainly has -OH and -O ligands and lacks -COOH ligands, whereas the -COOH ligands of the Ru dye will combine with the hydroxyl group of the TiO_2 particles to produce an ester and allow easy electron transfer to the TiO_2 conduction band to acquire a rapid electron-transport rate [17]. Another reason is the steric hindrance in the anthocyanin pigment, which affects the effective bond formation on the oxide surface of TiO_2. Therefore, there is lack of electron transfer from the dye molecules to the conduction band of TiO_2.

Table 1. Photovoltaic performance of the DSSC sensitized with the anthocyanin pigment with three different colours under acidic and non- acidic conditions.

Sample	Voc (V)	Jsc (mA/cm^2)	Fill Factor	Efficiency (%)
Pink	0.5516	0.8492	0.7201	0.33
Red	0.5439	0.8503	0.7231	0.33
Violet	0.5439	0.6938	0.7159	0.27
Pink+ CH_3COOH	0.5447	0.8879	0.7241	0.35
Red+ CH_3COOH	0.5380	0.9318	0.7291	0.36
Violet+ CH_3COOH	0.5417	0.7371	0.713	0.28
Pink+HNO_3	0.5255	0.7800	0.6902	0.28
Red+HNO_3	0.5222	0.7671	0.6876	0.27
Violet+ HNO_3	0.5238	0.7175	0.682	0.25

An acid treatment of the dye molecule was attempted to increase the power conversion efficiency. The fill factor for the pink, red and violet dye treated with nitric acid was 0.6902, 0.6876 and 0.682, respectively. The respective values for the acetic acid treated pink, red and violet dye was 0.7241, 0.7291 and 0.713. The fill factor for the bare and acetic acid-treated dyes was high compared to the nitric acid treated dye. The Jsc value of the nitrated pink, red and violet dye was 0.780, 0.767 and 0.717, respectively, whereas with the acetic acid treated, the Jsc increased to 0.887, 0.932 and 0.737, respectively.

Better performance was obtained with the acetic acid treatment than the nitric acid because nitric acid is a strong oxidatic acid compared to acetic acid. According to UV-Vis spectroscopy, although the color intensity of the dye solution increased with an acid treatment, the absorption spectra of dye adsorbed TiO_2 films of the bare and acetic acid-treated dye were similar. On the other hand, the cell performance was higher with the acetic acid-treated dye than the bare dye. In both cases, the absorption intensity was the same, which confirms that the acid treatment does not affect the dye molecules for more absorbance, but it modifies the TiO_2 surface. According to Jeong et. al (18), the acetic acid-treated TiO_2 showed more efficiency than the untreated TiO_2 because the acetic acid-modified TiO_2 films had a better morphology than the untreated TiO_2 film, resulting in an increase in cell performance due to the transportation of electrons. At the same time, the nitric acid-treated dye adsorbed TiO_2 film shows less absorption in the UV-Vis spectrum and poor performance in the power conversion efficiency. The nitric acid present in the dye modifies the surface state of the porous film and creates defect centers on the TiO_2 surface. These defects prevent the transfer of electrons to the TiO_2 grid from the excited state of the sensitized dye molecule, which results in lower electron transportation efficiency and a decrease photovoltaic performance [19]. Therefore, the efficiency was higher with the acetic acid-treated dye than the nitric acid and untreated dye. On comparing the efficiency of three different colored pigments the conversion efficiency of pink and red is on par with each other compared to the efficiency of the violet dye in both acid treated and untreated dyes.

4. CONCLUSION

The generation of photovoltaic currents was demonstrated by illuminating FTO electrodes coated with TiO_2 nanocrystalline film sensitized with anthocyanin pigments extracted from the three different colored flowers of Rhododendron species using a simple extraction technique. In UV-vis spectroscopy, the broad absorption peak of the pigments in the visible range revealed the adsorption of dye molecules to the TiO_2 nanoparticles. In FT-IR study, the peaks at $1726 cm^{-1}$ were assigned to C=O stretching vibration for all the three colors, indicating the partial appearance of the quinonoidal form of the anthocyanin in dye. The anthocyanin pigment treated with acetic acid provided better performance than the nitric acid-treated and bare dye. The short circuit current for the pink, red and violet acetic acid-treated dye was 0.887, 0.932 and 0.737 mA/cm^2, respectively. Among the three different colors, the pink and red dyes treated with acetic acid showed the highest conversion efficiency of 0.35 and 0.36% respectively, compared to the violet colored dye. Acid treated dye adsorption on TiO_2 film was expected to have more influence because of its high color intensity. On the other hand, the UV study revealed no significant changes in the absorbance spectra between the acetic acid-treated dye-adsorbed TiO_2 and the bare dye adsorbed TiO_2 film. On the other hand, the cell performance was good with the acetic acid-treated dye adsorbed TiO_2 compared to the other dye solution due mainly to modification of the TiO_2 surface and not to the color intensity of the dye solution. In general, natural dyes are promising alternative sources of sensitizers for DSSCs because of the simple extraction procedure, low cost, wide availability and environmentally-friendly nature.

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