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## A combined spectroscopic and TDDFT study of natural dyes extracted from fruit peels of *Citrus reticulata* and *Musa acuminata* for dye-sensitized solar cells

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### ABSTRACT

This study reports the novel spectroscopic investigations and enhanced the electron transfers of *Citrus reticulata* and *Musa acuminata* fruit peels as the photosensitizers for the dye-sensitized solar cells. The calculated TD-DFT-UB3LYP/6-31 + G(d,p)-IEFPCM(UAKS), experiment spectra of ultra-violet-visible spectroscopy, and Fourier transform infrared spectroscopy studies indicate the main flavonoid (hesperidin and gallicocatechin) structures of the dye extracts. The optimized flavonoid structures are calculated using Density functional theory (DFT) at 6-31 + G(d,p) level. The rutinosyl group of the hesperidin pigment (*Citrus reticulata*) will be further investigated compared to the gallicocatechin (*Musa acuminata*) pigment. The acidity of the dye extract is treated by adding 2% acetic acid. The energy levels of the HOMO-LUMO dyes are measured by a combined Tauc plot and cyclic voltammetry contrasted with the DFT data. The electrochemical impedance spectroscopy will be performed to model the dye electron transfer. As for the rutinosyl group presence and the acidic treatment, the acidified *Citrus reticulata* cell under continuous light exposure of  $100 \text{ mW} \cdot \text{cm}^{-2}$  yields a short-circuit current density ( $J_{sc}$ ) of  $3.23 \text{ mA/cm}^2$ , a photovoltage ( $V_{oc}$ ) of 0.48 V, and a fill factor of 0.45 corresponding to an energy conversion efficiency ( $\eta$ ) of 0.71% because the shifting down HOMO-LUMO edges and the broadening dye's absorbance evaluated by a combined spectroscopic and TD-DFT method. The result also leads to the longest diffusion length of  $32.2 \mu\text{m}$ , the fastest electron transit of 0.22 ms, and the longest electron lifetime of 4.29 ms.

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### 1. Introduction

Nowadays, the dye-sensitized solar cell (DDSC), first developed by Grätzel and O'Regan in 1991, is considered the prominent energy source because of its low fabrication cost [1]. In this cell, a photovoltaic commonly needs a titanium dioxide ( $\text{TiO}_2$ ) anatase structure as a photoanode sensitized by dyes in order to broaden the visible light spectrum absorption [2]. The application of natural dye especially extracted from waste materials of fruit peels as a photosensitizer source may ideally conserve the environment [3,4]. The utilization of natural dye pigments has many advantages for DSSC because it is easy to extract, biodegradable, nontoxic, abundant, and environment-friendly [2]. However, only few works have recounted the usability of fruit peels for the application of DSSC. Calogero and Di Marco first narrated eggplant peel pigment as a photosensitizer,

achieving the cell efficiency of 0.47% [5]. Zhou thereafter described tangerine peel as a photosensitizer, achieving the cell efficiency of 0.28% [6]. Eka subsequently reported the use of *Musa aromatica* peel as a photosensitizer, achieving the cell efficiency of 0.21% [7]. In accordance with the literature reviews conducted by Calogero [8], Bella [9], Hug [10], and Luddin [11], there is no further research reporting the usability of other fruit peels as photosensitizers in class of flavonoid group.

The present investigations and modifications of natural dyes based on the presence of donor groups have been employed in order to improve cell performance. Singh and coworkers [12] found that the higher the number of glucose moieties as donors in cyanidin dye, the better the photosensitization of the cells. Calogero and coworker [13] explicitly added the *N,N*-diethylamino as a donor moiety. This treatment improves the cell performance due to narrowing the dye's band gap and increasing the dye's dipole moment. Moreover, other treatments such as solvent effects [14–16], acid treatments [2], quantum dot coupling [17], dye combinations [18], dye purifications [19], and pure/combined TD-DFT-experiment [20–23] have also been employed to improve dyes' photosensitizations. In this work, a combined spectroscopic and TD-DFT

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method will be proposed to model the flavonoid dyes as photosensitizers in the DSSC system. The report shows the donor moiety investigation, the photo-induced electron transfer, the predicted open circuit voltage, and the light-harvesting efficiency. Therefore, this model will clarify the spectroscopic analysis and photochemical properties of DSSC.

Some varieties of rind have currently been scrutinized either as an antioxidant material to prevent free radicals, or a light-harvesting material with good photochemical properties. Hesperidin, 3',5,7-trihydroxy-4'-methoxy-flavanone-7-O- $\beta$ -rutinoside, is the major active constituent of bioflavonoid greatly found in *Citrus reticulata* peels (94 mg/100 g dry wt.) [24–27]. In nature, hesperidin has an ability to prevent some diseases, such as reducing capillary permeability, carcinogenic effects, inflammation, and microbial infection [25]. Moreover, researchers have also evaluated the antioxidant activity properties of this pigment using a variety of assay systems [25]. On the other hand, gallicocatechin or gallicocatechol pigments are more abundant flavonoids founded in *Musa acuminata* peel (158 mg/100 g dry wt.) than in its pulp (29.6 mg/100 g dry wt.) [28–31]. Banana peel has been considered a good source of antioxidants against heart disease and cancer [29]. Interestingly, gallicocatechin is also applied by industries to produce the anticorrosive agents [30]. Herein, we have investigated how the hesperidin dye-possessing rutinosyl moiety (6-O-(6-deoxy- $\alpha$ -L-mannopyranosyl)-D-glucose or O- $\alpha$ -L-rhamnosyl-(1  $\rightarrow$  6) glucose) as a natural donor of hesperetin will contribute to a better photosensitization effect than gallicocatechin. The dyes will be tested in neutral and acidic conditions. The dyes' electronic structures, the  $\pi \rightarrow \pi^*$  electronic transitions, the charge transfer properties, and the device characterizations will also be evaluated.

Fig. 1 illustrates the photosensitization process of both hesperidin and gallicocatechin dyes under illumination. The first time, the dyes as light-harvesting materials capture the light spectrum, initiating the  $\pi \rightarrow \pi^*$  electronic transitions. In a short time, electron injections from excited dyes captured by TiO<sub>2</sub> must dominantly occur while electron recombination captured by oxidized dye and electrolyte mediator must be extremely suppressed. The complete processes required by a cell in converting the solar energy circuit are described in Eqs. (1) through (5), respectively.

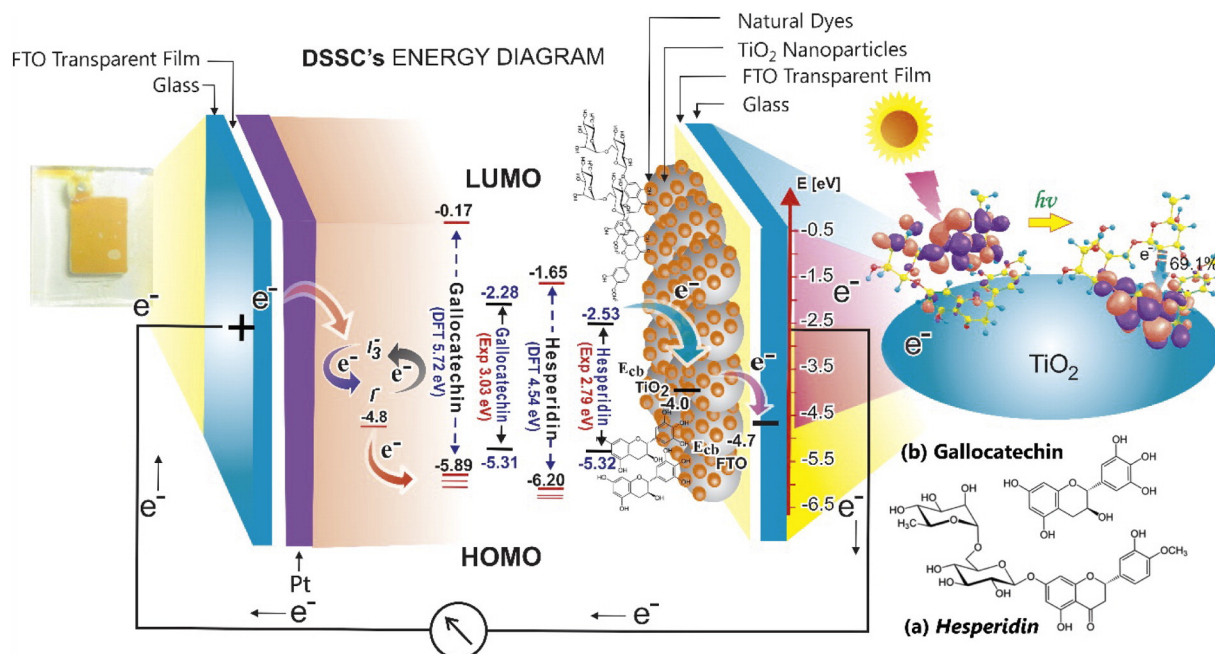
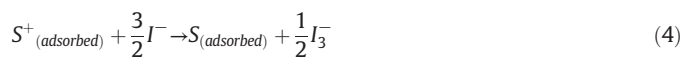
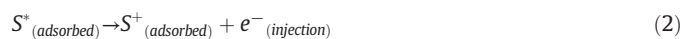


Fig. 1. The natural DSSC structure and its schematic reaction.



The photons first captured by dye molecules will stimulate ground-state dyes to an excited-state condition, as shown in Eq. (1). The higher level of the dye's lowest unoccupied molecular orbital (LUMO) band edge above the TiO<sub>2</sub> conduction band is needed in order to facilitate fast electron injections. The dye oxidation process will leave a positive dye ion (S<sup>+</sup>), as shown in Eq. (2). To regenerate this oxidized dye, Eqs. (3) and (4) show how the electrolyte mediator supplies electrons for returning to the ground-state condition of dye. However, the electron transfer from iodide ion will affect the formation of tri-iodide ion. Finally, the electron will be captured again by the tri-iodide ion in order to form iodide ion again, as shown in Eq. (5). The electrochemical impedance spectroscopy analysis is adopted to evaluate the intermolecular electron transfer dynamic as well as the electron recombination phenomena, as outstandingly described by Bisquert and coworker. This study will attempt to analyze the electron transfer properties and the electron recombination due to the presence of the rutinosyl group in the flavonoid structure.

Fig. 2 presents the chemical structures of gallicocatechin, hesperidin dyes, and their possible bidentate bridging mode of dye-TiO<sub>2</sub>. These natural dye pigments are responsible for orange colors. According to these flavonoid structures, both the catechol moiety in ring B and the benzopyrone systems in ring A/C containing a single-double bond conjugated structure facilitate good electron transfer. The presence of hydroxyl and carbonyl groups will facilitate dye binding onto the TiO<sub>2</sub> surface. Ambrosio reported that the dyes' bidentate chelating mode will provide more stable binding than the monodentate mode [32,33]. Sang-aron reported [23] that the nearest distances between the anchoring moiety and the LUMO site will affect the highest probability of the dye chelating onto the TiO<sub>2</sub> surface. Further investigation into this dye-chelating mode will be elucidated in the following discussion.

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