Aqueous Extract of Onion Peels as A Biowaste-Based Sensitizer for Photovoltaic Cells

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Abstract: In the present paper, two natural photosensitizers extracted from red onion peels have been experimentally studied to sensitize the photovoltaic cells. The two natural dyes were prepared overnight, soaking the red onion peel powder in distilled water without acidification (UW) and acidified water (AW). Dye characteristics were identified by UV-visible Spectrophotometer and FT-IR Spectrophotometer. The cell performance was assessed by calculating the produced voltage and current by multi-meter. Red onion peel dyes absorb visible light at a wavelength of 507 nm and promote electron transfer into the porous semiconductor surface. A higher power conversion efficiency (η=0.0535 %) was featured by an unacidified solvent with a short circuit current density (Jsc) of 0.96 mA.cm^-2, an open circuit voltage (Voc) of 338 mV and a fill factor of 0.2576. This paper presents a fascinating preliminary study to develop renewable and sustainable energy sources using bulky biowaste.

Keywords: Aqueous extracts, biowaste-based sensitizer, onion dyes, photovoltaic cells.

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1. INTRODUCTION

Energy crises, fossil fuel depletion, and environmental issues encourage researchers to strive for sustainable and renewable energy sources. One of the efforts is to utilize solar radiation, which is abundant, accessible, and eco-friendly. Solar radiation provides energy of $3 \times 10^{24}$ J per year to the Earth or about ten thousand times more than the world population demands (1). Solar cells, also called photovoltaic cells, can be used to utilize this freely available energy. The key parameter in harvesting solar energy is the capability of the cells to transform solar radiation into electrical power.

Dye-sensitized solar cells (DSCs) represent a promising device for directly converting solar radiation. It can be fabricated cheaply and produces high power conversion efficiency. This device involves a photoelectrochemical process to convert solar radiation into electrical power based on the sensitization of wide-band gap semiconductors. Generally, the DSSCs structure comprises a photoanode, dye molecules or sensitizer, a redox electrolyte, and a counter electrode as cathode (2–4). The dye sensitizer is the main component in capturing solar radiation and transforming it into electrical power (5). To enhance the DSSC performance, a dye sensitizer should have absorption from UV-visible to near-infrared spectrum and contain carboxyl and hydroxyl groups required for proper binding to the semiconductor (6,7). The functional groups promote negative charge transfer into the TiO2 conduction band; thus, the power conversion capability of DSSC can be improved.

Ruthenium complexed with carboxylated polypyrrold ligands is a synthetic inorganic sensitizer with the highest power conversion efficiency of 11%-12% (8,9). However, due to the high cost and tedious manufacturing method, sensitizer-based natural dyes are considered a favorable option for DSSC devices. Sensitizer-based natural dyes can be safely...
prepared at a low cost from flowers, fruits, and plants (3). Using biowaste-based materials as natural dye sources is important due to their seasonal independence, uncompetitive-to-food products, and eco-friendly properties. Biowaste-based materials have shown significant advantages in utilization as natural sensitizers (1,10,11). Red onion peel, an abundant biowaste from agroindustry, has drawn significant attention as a novel raw material for photosensitizer purposes. This waste occurs in huge quantities because onion is a daily-consumed staple from the household to the restaurant. Anthocyanin is one of the natural pigments easily found in onion biowaste. It is a watery soluble compound and contains carbonyl (C=O) and hydroxyl group (OH) that can be absorbed to the TiO$_2$ surface and stabilize the excited states (12–14). Anthocyanin shows a wide absorption band in the visible light spectrum and accelerates the electronic transitions of the dye molecules. Onion peel analysis exhibits a high anthocyanin content (15,16), making it possible to apply as a natural, affordable, and sustainable sensitizer.

An important parameter to prepare the pigment is the choice of extracting solvent. Various extracting solvents can affect the absorption spectrum of natural pigments as well as the bonding between the pigments and the TiO$_2$ surface (17). Acidified ethanol: water mixture (1) as extracting solvent of red onion peel dyes gives a higher efficiency than ethanol and acidified ethanol (18) as much as 0.29%, 0.049%, and 0.0034%. Additionally, previous studies have found that combinations of ethanol and water encourage widespread visible spectrum absorption between 490 and 532 nm. The current study evaluated the effectiveness of acidified and non-acidified water as extracting solvents. Two different types of red onion peel extracts were used as photosensitizers to create dye-sensitized solar cells. The power conversion efficiencies were calculated using a UV-vis and FT-IR spectrometer to examine the extracted dyes' absorption properties.

2. EXPERIMENTAL SECTION

2.1. Material
The types of equipment used for the research are FT-IR Spectrometer Bruker Alpha, UV-vis Spectrophotometer (Genesys 10S Thermo Scientific), blender, water bath, solar simulator (ORIEL S013A), and I-V meter (Keithley 2400). The materials are acetonitrile (99.8%, Merck), distilled water, HCl 37%, TiO$_2$ (99.5%, Merck), KI (99.7%, Merck), I$_2$ (99.8%, Merck) and 4-pyridinecarboxylic acid hydrazide (97%, Merck).

2.2. Dye Extraction and Characterization
Onion peels were randomly taken from local food stalls. Onion peel dyes were prepared by grinding the sample in a mixer and sieving with a size of 200 mesh. The peel powder (100 g) was mixed with unacidified water (250 mL) and macerated for 24 hours in the chamber that was stored away from direct sun rays. The macerated solution was separated from the solids by using Whatman Filter paper, concentrated at 40 °C on a hot plate, and used to fabricate solar cells. The same procedure was carried out against the acidified distilled water. Both extracts were labeled as AW (acidified water) and UW (unacidified water). The dye absorption band against UV and visible light was characterized by UV-vis spectrophotometer; meanwhile, the functional groups were analyzed by FT-IR spectrometer.

2.3. DSSC Fabrication and Performance
The present DSSC was prepared according to our earlier study (19). DSSC device was assembled from four main components (photoanode, nature-based sensitizer, electrolyte solution, and auxiliary electrode). TiO$_2$ paste was printed to the conductive side of Indium Tin Oxide/ITO glass to prepare the working electrode. TiO$_2$-coated glass was dehydrated for 15 minutes at 120 °C in a bath. TiO$_2$-coated glass was annealed at a temperature of 500 °C for 1 hour. This working electrode was subsequently immersed for 20 hours in aqueous extracts of red onion dyes and then washed with C$_6$H$_5$OH. The stained electrode was gently dried at 80 °C on a water bath for further use in dye sensitization. To prepare a redox electrolyte solution containing iodine and potassium iodide, KI, I$_2$, and 4-pyridinecarboxylic acid hydrazide were dissolved in acetonitrile; meanwhile, the cathode was fabricated by painting the glass slide with synthetic graphite. The graphite-painted slide was covered through screen printing with Graphite: PANI (3:1) paste. It was heated at 120 °C for 15 minutes before being allowed to cool at room temperature. Before examining the DSSC performance, electrolyte solution was injected into the working electrode, and two binder clips were used to clamp the photoanode and counter electrode. These DSSCs were set under irradiation of light (100 mW) using a solar simulator (ORIEL S013A), whereas the current and voltage were measured by a Keithley 2400 I-V meter. Photovoltaic cell performance in terms of energy-transforming efficiency was determined using the equation according to Richhariya et al. (2) as follows:

$$\eta \% = \frac{J_{sc} \times V_{oc} \times FF \times P_{in} \times 100}{Pin}$$

where $J_{sc}$ is the short-circuit photocurrent (mAcm$^{-2}$), $\eta$ is the cell efficiency (%), $V_{oc}$ is open-circuit voltage (V), FF is the fill factor, and $P_{in}$ is the power of the solar simulator lamp (100 mW).

3. RESULTS AND DISCUSSION

3.1. Dye Extraction
Red onion (Allium cepa L.) has a red color peel and dry peel characteristics. Red onion contains anthocyanins and phenolics in the dry outer skin and epidermis layer (20,21). Anthocyanin can be extracted from onion peel through several
extracting methods, i.e., maceration, reflux, percolation, and soxhletation (22,23). Maceration was considered a suitable extracting method in this work because of its effectiveness in cell lysis, less solvent consumption, longer solvent-solute interaction, and lower temperature demand. Saptarini and Herawati (24) achieved a higher total anthocyanin content through the immersion method (maceration and reflux extraction) compared to the flowing solvent method (percolation and soxhlet methods). The choice of anthocyanins extracting solvent predominantly affects the total anthocyanin level. Anthocyanins are a group of water-soluble flavonoid compounds; therefore, distilled water was chosen as the proper solvent. Ali et al. (25) stated that onion peel extraction using acidified ethanol (0.01% HCl) gave a higher efficiency than acidified methanol (0.01% HCl). pH solution was reported elsewhere as another important factor that can affect the color stability of anthocyanin. Natural anthocyanin extracts showed the greatest stability at lower pH (2.0 and 3.0) (26,27). Therefore, an acid solution (0.01% HCl) was added to the distilled water in the current work (Figure 1) to stabilize the flavlylium cation, which is stable in highly acidic conditions.

3.2. Dye Absorption

UV-visible light absorption capacity of the natural sensitizer and the transport of expelled electrons through the porous TiO₂ film determine the overall performance of DSSC. The absorption capability of the extracted onion peel dyes was measured using a UV-vis spectrophotometer between the wavelength of 400 to 780 nm and illustrated in Figure 2. There are two identical absorption peaks in the visible spectrum with a maximum absorption of 507 nm featured by extracted onion peel dyes, both unacidified and acidified water. These intense wide-band absorptions in the visible spectrum approximately meet the value noted by Hosseinnezhad et al. (28) for extracted anthocyanin from onion peel using ethanol (508 nm). However, they are slightly different from the maximum absorption reported by Ammar et al. (10) and Adoloju (1) using water (486 nm) and the mixture of ethanol-water (532 nm) as extracting solvent, respectively. Absorption peak difference is attributed to the different quantities of functional groups and the color of extracted anthocyanins. Moreover, the presence of unnecessary particles potentially resulted in different absorption.

In the present work, the two extracted dyes (AW and UW) absorb visible light photons, resulting in $n \rightarrow \pi^*$ and $\pi-\pi^*$ transition. The absorption capability of these extracts is responsible for the efficient conversion of photons into electrical power in DSSC. Photon absorption leads to the generating of excited electrons from HOMO to LUMO (29,30). The presence of anthocyanins functional groups in the extracts allows their adsorption into the TiO₂ surface (Figure 4). This adsorption promotes the electron transfer from the dye to the TiO₂ conduction band, ultimately improving the DSSC power conversion efficiency.

Figure 1: Workflow of The Current Work.

Figure 2: UV-vis Absorption of Extracted Red Onion Peel Dyes.
In order to effectively adsorb in TiO$_2$ surface, the dye sensitizer needs to have specific functional groups. Functional groups contained in onion peel extracts were identified by FT-IR Spectrometer at a wavenumber of 4000-500 cm$^{-1}$. Figure 3 reveals identical absorption of the two extracts.

The absorption band in the 3402 and 3425 cm$^{-1}$ wavenumber is attributed to the –OH strain vibration. The absorption band of C=C strain vibration aromatic and C-H aromatics is observed in the wavenumber of 1651 and 655 cm$^{-1}$. The C–O group is detected at 1041 cm$^{-1}$; meanwhile, the C–H strain appears at wavenumber 2854 and 2924 cm$^{-1}$ for C–H$_{3}$ and C–H$_{2}$. Absorption peak showing C=O vibration that is characteristic of anthocyanin is detected in UW extract (1735 cm$^{-1}$) but totally disappears in the AW spectra, presumably due to the rapid transformation of C=O groups into –O– groups under acidic conditions. The presence of these groups is similar to the previous report (10,27,28). According to Swer et al. (31) the presence of O–H, C=O, C=C, and C–O–C functional groups in the FT-IR spectra is the absorption characteristic of anthocyanin compounds; therefore, onion peel extracts in this study have characteristics as an anthocyanin. These specific functional groups possess anchoring capability on the TiO$_2$ layer, promoting a high electron transfer rate. The different absorption intensity of the two extracts is also confirmed by FT-IR Spectra. Under acidic conditions, functional groups absorb less intensely than in nonacidic conditions because of pigment degradation during extraction. As previously reported, pigment degradation can occur in unstable residues of acyl groups and sugars because of acid hydrolysis (32).

3.3. DSSC Performance

As revealed in Figure 4, the present photovoltaic solar cell was arranged by an opposite electrode (conductive glass covered with platinum), photoanode (conductive glass coated with TiO$_2$ film), dye and electrolyte solution (redox pairs I$^{-}$/I$_3$-) (14). In order to examine the prepared onion peel dyes as a natural photosensitizer, the DSSC device was fabricated by varying the extracts (acidified water extract and unacidified water extract). The addition of a low content of hydrochloric acid (0.01%) in the present work may improve the stability of the produced flavylvium ion in an aqueous solution. Generally, the effective light exposure domain of the DSSC was retained at 1 cm$^2$; meanwhile, the I$^{-}$/I$_3$ solution and Pt thin film were used as the redox mediator and the counter electrode, respectively.
The photovoltaic variables such as short-circuit photocurrent density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and total power conversion efficiencies (%) for the aqueous extract of onion peels are summarized in Table 1. These parameters are determined by measuring the photocurrent–voltage (J–V) curves which are displayed in Figure 5. The power conversion efficiency of the fabricated cell mainly depends on two key variables: open circuit voltage and short circuit current. Short circuit current production primarily relies on the quantity of adsorbed dyes on the porous TiO$_2$ device framework, sunlight converting efficiency, and capability of the prepared dye to accelerate electron injection (3). The more adsorbed dye molecules on the surface site of TiO$_2$, the more the generated photons that are heading to the rapid electron flow (33,34).

On the other hand, the open circuit voltage or output voltage was defined as the difference between the quasi-Fermi level of free electron of the TiO$_2$ electrode and the redox couple potential of mediator, which mostly counts on the recombination rate of electron and adsorption mode of the prepared sensitizer (29,35). In this work, photovoltaic cells based on the unacidified extract of onion peels performed the better power conversion efficiency of 0.0535%, whereas the other exhibited efficiency of 0.0021%. The cell’s efficiency is still low because of a lower fill factor than normal values. The fill factor value in this study is only influenced by the $J_{sc}$, and the $V_{oc}$ value does not affect the FF because of the use of the same redox pair and semiconductor. To achieve the proper $V_{oc}$ value, active layer which is dye with high band gap is needed. Generally, natural pigments which act as DSSC photosensitizers exhibited lower power conversion efficiencies than that of synthetically prepared dyes owing to the less presence of particular functional groups (36).

A higher power conversion of the photovoltaic device based on unacidified water extract is attributed to the high presence of extracted anthocyanin containing hydroxyl and carbonyl groups. The more content of functional groups may amend the maximum electron injection into the TiO$_2$ surface by the chemical adsorption process. In contrast, the acidified aqueous extract of onion peels has less quantity of adsorbing functional groups, as featured in Figure 3, due to the
The measured power conversion efficiency of unacidified water in our present device is higher than that of our previous photovoltaic cells when unacidified methanol and ethanol were used as extracting solvent (0.0413 and 0.0491 %) (18,19). It was reported elsewhere that anthocyanins are highly soluble in water. Their polyphenolic compounds increase the hydrophobic characteristic, which makes them soluble in organic solvents (38). Furthermore, compared to recently reported natural sensitizers using similar samples and solvents, our power conversion efficiencies of the produced devices are slightly inferior (1,28). Its different efficiency could be due to the different treatments applied to the crude extract. It appears that adding the purification stage using hexane and adjusting the temperature to 90 °C, as performed by previous workers, is highly needed to improve the efficiencies. Therefore, it is suggested to optimize the other analytical parameters in the future, such as extraction pH and time, powder size of the solid, and solvent-to-solid ratio, in addition to the purification and temperature to ensure the maximum yields of anthocyanins.

4. CONCLUSION

Two extracted dyes from onion peels were examined as natural photosensitizers in DSSC. The aqueous extracts of onion peel dyes can transform solar radiation into electrical power through a photoelectrochemical solar cell. The acidified and unacidified extracts have anchoring groups and strongly absorb the visible spectrum at 507 nm. The DSSC device assembled from the unacidified red onion peel dye extract demonstrated a higher power conversion efficiency of 0.0535% than the acidified extract.

5. CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

6. ACKNOWLEDGMENTS

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7. REFERENCES

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