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Impact of Various Solvents on Extraction of Anthocyanins from Blueberry for Use in Dye-sensitized Solar Cells

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We extracted anthocyanins from a natural dye source, blueberry, by a solvent extraction method for use as sensitizers in the fabrication of dye-sensitized solar cells (DSSCs). In the extraction of anthocyanins, we used solvents such as acetonitrile, tert-butanol, ethanol, and acetone, and their effects on the performance of DSSCs were examined. Currently, the available commercial-grade titanium dioxide (TiO_2) powder is composed of 80 mol% rutile and 20 mol% anatase phases. In the preparation of the photoanode, the TiO_2 powder was applied by a doctor blade technique. The prepared photoanodes were immersed in the extracted anthocyanin dye and exposed for different durations while being shielded from light throughout the process. To prepare electrodes, a platinum film approximately 1 nm thick was sputter-coated onto an indium tin oxide (ITO) glass substrate. Finally, the coated photoanodes were sealed with the electrode by dye-soaking. To evaluate the performance of the fabricated DSSCs, the incident photon-to-electron conversion efficiency (IPCE) was measured by ultraviolet-visible spectroscopy (UV–VIS) and a solar simulator. The results showed that DSSCs with the dye extracted from blueberry in tert-butanol for 12 h showed the best efficiency. In this study, tert-butanol was the best extraction solvent for the fabrication of DSSCs with anthocyanins extracted from blueberry with an efficiency of 0.45% and a fill factor of 68.20%. Further study is required to find a more appropriate solvent and extraction method, while the result of this study proved that the use of a dye from a natural dye source such as blueberry in solar cell technology is promising.

1. Introduction

Dye-sensitized solar cells (DSSCs) require conductive glass, commonly referred to as transparent conductive oxide (TCO), as a material for electrodes. TCO films play a pivotal role in DSSCs. Tin dioxide (SnO_2) and indium tin oxide (ITO) are known as the best TCO materials owing to their exceptional transparency and strong electrical conductivity.(1,2) However, the sheet resistance of ITO films tends to increase at elevated temperatures, whereas films made of fluorine-doped tin oxide (FTO) exhibit smaller impedance changes. As a result, high-

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temperature annealing is frequently utilized in the fabrication of dye-sensitized solar cells with titanium dioxide (TiO_2). Therefore, FTO is more frequently used.(3,4) The appropriate use of ITO or FTO substrates in fabricating DSSCs is significant as the substrate material affects the overall performance and stability of DSSCs, which are influenced by temperature variations and the annealing process. Electrode materials affect the sensitizing properties of TiO_2 and the overall design and optimization of DSSCs.

In DSSCs, the photoanode plays a crucial role in adsorbing dye molecules and facilitating charge transfer. Common materials of the photoanode include TiO_2,(5) ZnO,(6) and SnO_2,(7) where TiO_2 is the most widely used. TiO_2 powder exists in three crystal structures: anatase, rutile, and brookite. TiO_2 powder with an anatase phase exhibits excellent light scattering properties, which allows for enhanced light absorption, whereas TiO_2 powder with a rutile phase has lower electron transport resistance but promotes efficient electron transfer on the surface TiO_2. As a result, TiO_2 nanoparticles in both crystal phases are used in DSSCs. The currently commercially available TiO_2 powder is prepared with 80 mol% rutile and 20 mol% anatase phases. This combination allows for efficient light absorption and electron transport as a photoanode material, and their crystalline structures are pivotal in the performance and efficiency of DSSCs. Therefore, researchers and engineers continually explore combinations and modifications of materials for the photoanode to enhance solar energy conversion, which is presently a key focus in advancing this renewable energy technology.

Currently, the most commonly used material for the sensitizer is ruthenium-based dyes such as N3, N719, Black dye, and others. They have such advantages as high light absorption capability, photoconversion efficiency, and photostability. However, there are also the drawbacks of the rarity, high cost, and toxicity of ruthenium as well as the environmental impact of its extraction and production. Consequently, researchers are increasingly exploring the use of natural dyes as sensitizers,(8,9) among which anthocyanin and chlorophyll dyes have attracted much attention. Using natural dyes as sensitizers offers the following benefits in fabricating DSSCs.

(a) Environmental benefits: Natural dyes are derived from natural sources such as fruits, vegetables, or plants. Their extraction processes are less harmful to the environment than the chemical synthesis of ruthenium-based dyes.
(b) Cost reduction: Natural dyes significantly reduce the cost of manufacturing solar cells, making them more affordable for popular use.
(c) Sustainability: Natural dyes align with the principles of sustainability and renewability. They are also eco-friendly and appropriate for eco-conscious approaches in renewable energy technologies.
(d) Biocompatibility: Natural dyes are biocompatible and bio-photovoltaic, making them suitable for wearable solar devices.

Kokkonen *et al.* stated that DSSCs are capable of powering electronic applications such as wireless sensors and indoor lighting as an efficient photovoltaic technology.(10) Lokhandea *et al.* synthesized zinc oxide (ZnO) films by a chemical bath deposition method and explored various deposition mechanisms for manufacturing gas sensors and DSSCs.(11) In accordance with the expansion of DSSC applications, the use of natural dyes for the manufacture of DSSCs is becoming more promising than before. However, there are challenges that need to be overcome in the use of natural dyes; in particular, ruthenium-based dyes do not always guarantee an increase in efficiency and stability with prolonged exposure to light. The environmental effect of extracting ruthenium-based dyes is also a concern in its manufacture. Therefore, researchers have tried to address such issues in attempts to find appropriate natural-dye-based sensitizers. Such efforts have resulted in the development of renewable energy technology for better sustainability, cost-effectiveness, and less environmental impact.

Anthocyanins belong to the natural pigment group known as flavonoids. Depending on the number and position of methoxy (OCH_3) or hydroxyl (OH) groups, they are categorized into delphinidin, petunidin, pelargonidin, peonidin, cyanidin, and malvidin. Previous research results showed that TiO_2 bonds with anthocyanins, allowing anthocyanins to be used as natural dyes in fabricating DSSCs.(12) Therefore, we extracted anthocyanins from blueberry juice in different solvents and used them to investigate how different solvents affect the characteristics of the extracted anthocyanins and eventually influence the performance of DSSCs. The effect of the type of solvent on the final properties and performance of DSSCs was investigated to prove the advantage of the use of anthocyanins as sensitizers in solar cell technology.

2. Fabrication and Measurement

A DSSC requires ITO and FTO glasses for the photoanode and a counter electrode, respectively. In the fabrication of DSSCs in this study, ITO and FTO conductive glasses were cut to 1.5×3 cm^2 in size. The substrates were then immersed in a dish containing acetone and ultrasonicated to eliminate oils and impurities on the surface. Then, they were immersed in isopropyl alcohol and ultrasonicated again for 10 min to remove residual oils and impurities. Subsequently, the substrates were washed in deionized water and ultrasonicated for 10 min to remove organic solvents completely. The substrates were dried first by blowing nitrogen gas over their surfaces, and then in an oven at 50 °C for 30 min.

To extract natural dyes, blueberries were ground in a mortar and mixed with solvents for extraction. Six different extraction solvents were used, namely acetonitrile, tert-butanol, ethanol, acetone, acetonitrile mixed with tert-butanol, and ethanol with acetone. The solvents were prepared at a concentration of 200 g/L to ensure uniform dye concentration. The extracted dye solution was transferred into a glass container and heated while stirring on an electromagnetic heating stirrer. The extracted dye was then filtered to remove solid residues. To prepare the electrodes, the previously cleaned, dried, and perforated ITO glass was placed in the sputtering chamber of a gold-plating machine. In the chamber, vacuuming and sputtering were performed for 60 s at a current of 10 mA. The thickness of the sputtered platinum (Pt) was approximately 10 nm. This counter electrode was used for DSSCs.

The electrolyte was prepared by mixing the following materials in 3-methoxypropionitrile (MPN): 0.1 M lithium iodide (LiI), 0.05 M iodine (I_2), 0.5 M 4-tert-butylpyridine (TBP), and 1 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII). The solution was then ultrasonically agitated. To prepare the photoanode slurry, tert-butanol, TiO_2 nanoparticles, and deionized water were mixed to a 10 wt% concentration, and the mixture was stirred for at least 6 h. The photoanode was fabricated by a doctor blade method. Initially, the cleaned and dried FTO glass was placed on a custom-made holder until the required thickness of the TiO_2 film on the glass was acquired. Once the film was dried completely in air, it was pressurized at 20 kg/cm^2 for 60 s. The FTO glass with the TiO_2 film was then heated in a high-temperature annealing furnace at 150 °C for 1.5 h, followed by heating at 550 °C for 30 min. Finally, the annealed TiO_2 film was exposed to UV light for 10 min to remove impurities generated during annealing.

After the annealing process, the photoanodes were immersed in different natural dyes for 6, 12, or 24 h. The entire process was conducted in the dark to avoid exposure to sunlight. Any remnant dye on the photoanodes was removed using the appropriate solvent. In the encapsulation of DSSCs, we used a 0.06-mm-thick thermoplastic polymer film. This film was cut to a size of 2 × 1.2 cm^2 with a photoanode working area of 0.6 × 0.6 cm^2. The holes were drilled on the lower edge of the photoanode, and then the photoanode was placed on a sealing heating platform for encapsulation. A rudimentary sandwich structure was formed for DSSCs. Subsequently, the electrolyte was injected into the holes using a syringe. Then, the holes were sealed with a thermoplastic polymer film and an ITO glass, completing the package of the DSSC, as illustrated in Fig. 1. Ultraviolet-visible spectroscopy (UVS) was used to analyze the absorbance spectra of anthocyanins in different solvents. After a DSSC was packaged, the incident photon-electron conversion efficiency (IPCE) was measured to analyze the absorbed light of the DSSCs at various wavelengths. A solar simulator was used to measure the efficiency of the DSSC in generating electrical energy.

3. Results and Discussion

Figure 2 shows that the dye extracted from blueberry in pure acetone displayed the lowest absorption peak at 660 nm, whereas the dye extracted in acetonitrile did not exhibit any peak. In contrast, the dye extracted in the other four solvents (tert-butanol, ethanol, acetonitrile mixed with tert-butanol, and ethanol) revealed two prominent absorption peaks at 550 and 660 nm, signifying the presence of anthocyanins. These analysis results indicated that there were specific compounds responsible for the observed absorption patterns. Such information is pivotal in the applications of natural dyes since the amount of included anthocyanins is important for solar cell sensitization and even in food science. The results also underscored the importance of using appropriate solvents in the extraction process to optimize the yield and quality of the extracted compounds.

The efficiency of DSSCs depends on the light-absorbing capabilities of the photosensitizer and the efficiency of electron transfer and diffusion through the TiO_2 film. Figure 3 illustrates the UV–VIS spectra of TiO_2 films with dyes extracted in different solvents. The increased absorbance indicated the anchoring of dye molecules on the TiO_2 film and related chemical interactions. The quality of extracted dyes varied in accordance with the solvent. The tert-butanol-extracted dye displayed the highest absorption intensity, whereas the acetone-extracted dye showed a lower absorption. The lower absorption of the dye extracted in acetone was caused by the low chemical stability (easy volatilization) of acetone, which resulted in a limited reaction to extract anthocyanins.

Figure 4 shows the IPCE results of DSSCs with dyes extracted in different solvents. The efficient anchoring of anthocyanins to the TiO_2 film is crucial for enhancing light absorption

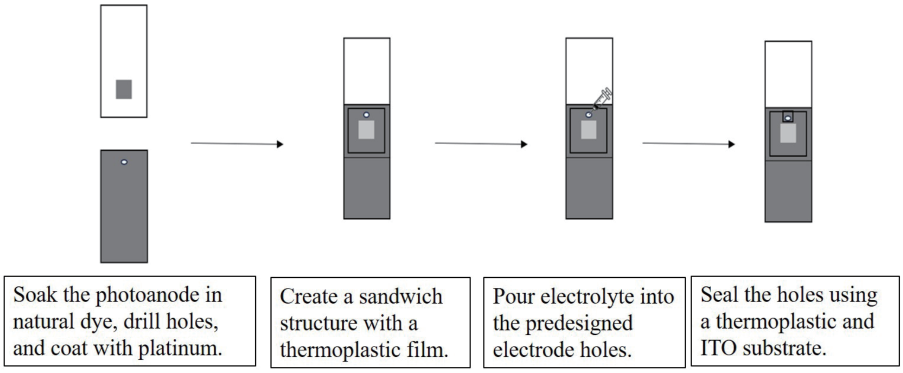

Fig. 1. DSSC encapsulation process.

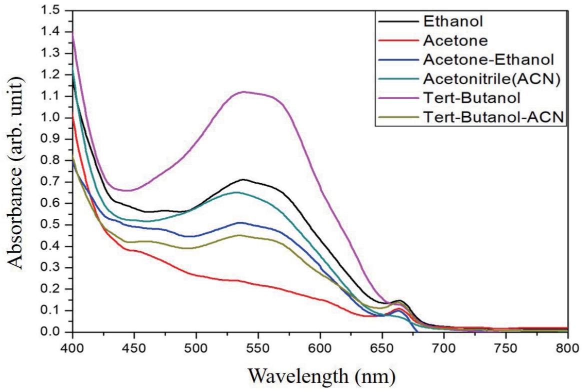

Fig. 2. (Color online) UV–VIS spectra of dyes extracted from blueberry in different solvents.

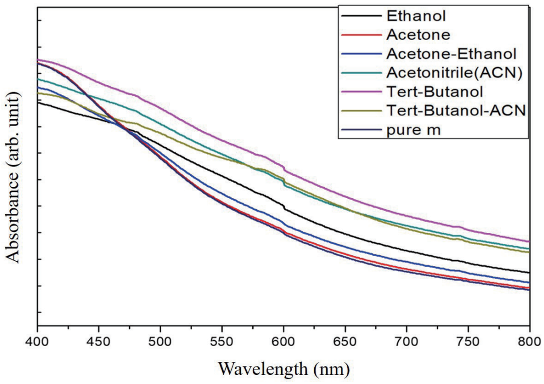

Fig. 3. (Color online) UV–VIS spectra of TiO_2 dipped in different solvents.

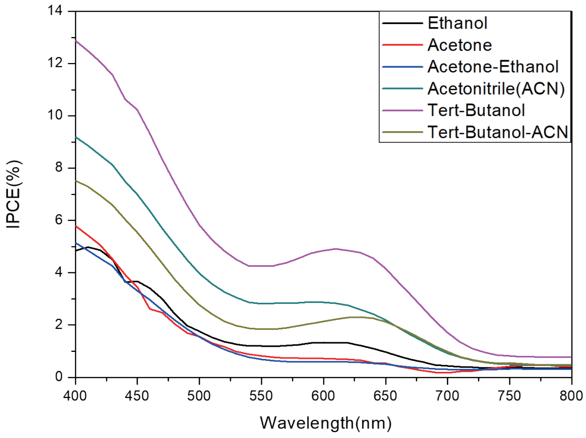

Fig. 4. (Color online) IPCE results of DSSCs with dyes extracted in different solvents.

and, in turn, the overall efficiency of DSSCs. IPCE is measured to understand how the dye of the DSSC absorbs light that is converted by solar cells into current at various wavelengths. In an ideal IPCE graph, the shape of the curve mirrors the UV absorption spectrum, indicating whether the dye efficiently converts light at different wavelengths into photocurrent. Absorption peaks in the UV absorption spectrum differ from those in the IPCE graph and indicate a low efficiency of the dye in converting light into electricity, significant resistance in electron transfer, or a rapid return of electrons to their ground state after excitation. This last phenomenon is known as electron–hole recombination. Thus, IPCE is a crucial indicator for assessing the effectiveness of dye sensitization in solar cells and shows the percentage of photons converted into electrons in different wavelength ranges. The light intensity does not significantly affect the IPCE of a solar cell.

We compared the light absorption efficiencies of the dyes extracted in different solvents. The tert-butanol-extracted dye showed the highest IPCE with light absorption efficiency reaching up to 13%. This value was 2.6 times higher than that of the dyes extracted in ethanol or acetonitrile mixed with tert-butanol. Tert-butanol extracted the most anthocyanins, which enhanced the light absorption efficiency and improved the performance of DSSCs. This indicated that the photoanode captured more photons and generated more electrons, resulting in an increased output current.

As the key factor of cell efficiency is current density, we analyzed the I-V characteristics of DSSCs fabricated with dyes extracted from blueberry in different solvents for 6, 12, and 24 h (Figs. 5 to 10). The results are presented in Table 1. It was found that extraction time influenced the overall performance of DSSCs. The highest efficiency was obtained with the dye extracted for 12 h. The efficiency decreased with the dye extracted for 24 h. The highest cell efficiency of 0.45% and fill factor of 68.20% were observed for DSSCs with the dye extracted in tert-butanol. The factor for efficiency degradation of extraction longer than 12 h was dye decomposition. As natural dyes are susceptible to decomposition, excessive extraction time led to dye decomposition, resulting in a reduction in cell efficiency. Additionally, the thickening of the dye layer owing to prolonged extraction also affected the efficiency. An overly thick dye layer

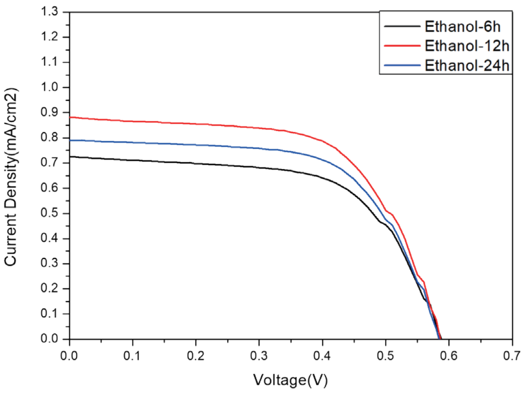

Fig. 5. (Color online) *I*–*V* characteristic curves of DSSCs with dye extracted in ethanol.

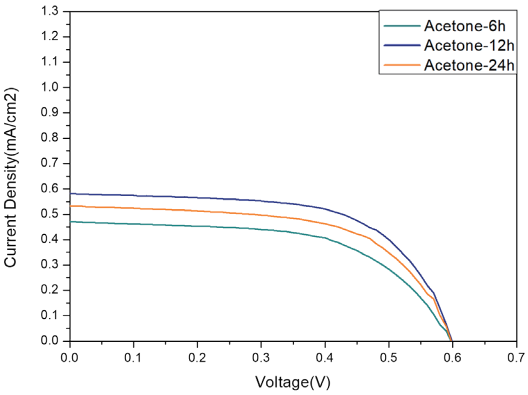

Fig. 6. (Color online) *I*–*V* characteristic curves of DSSCs with dye extracted in acetone.

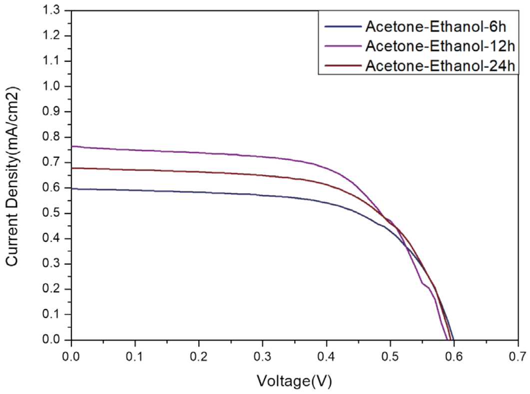

Fig. 7. (Color online) *I–V* characteristic curves of DSSCs with dye extracted in ethanol-acetone mixture.

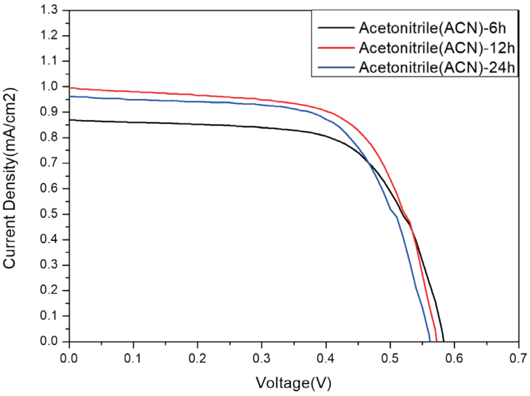

Fig. 8. (Color online) *I–V* characteristic curves of DSSCs with dye extracted in acetonitrile.

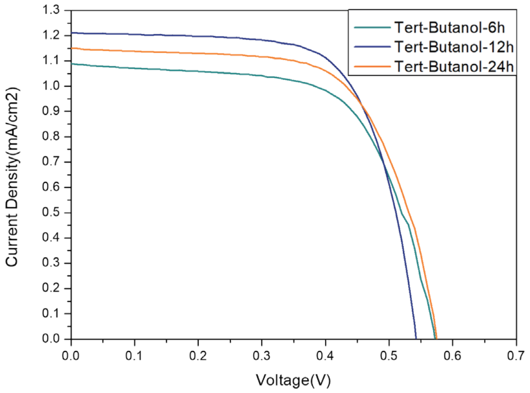

Fig. 9. (Color online) *I–V* characteristic curves of DSSCs with dye extracted in tert-butanol.

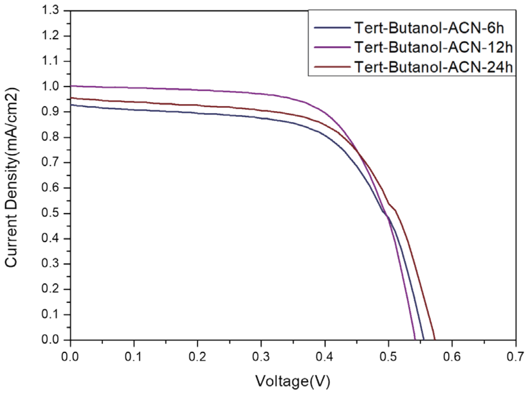

Fig. 10. (Color online) *I–V* characteristic curves of DSSCs with dye extracted in -tert-butanol with acetonitrile.

Table 1
J–V characteristics for blueberry dye with different extraction solvents and extraction times.

Sample	Voc (V)	Jsc (mA/cm^2)	Fill Factor (%)	Efficiency (%)
Ethanol-6H	0.59	0.73	61.27	0.26
Ethanol-12H	0.59	0.88	61.65	0.32
Ethanol-24H	0.58	0.79	62.79	0.29
Acetone-6H	0.60	0.47	58.16	0.16
Acetone-12H	0.60	0.58	61.47	0.21
Acetone-24H	0.60	0.53	60.02	0.19
Acetone-Ethanol-6H	0.60	0.60	62.93	0.22
Acetone-Ethanol-12H	0.59	0.77	60.98	0.27
Acetone-Ethanol-24H	0.59	0.68	62.61	0.25
Acetonitrile-6H	0.58	0.87	65.93	0.33
Acetonitrile-12H	0.57	1.00	65.69	0.37
Acetonitrile-24H	0.56	0.96	65.43	0.35
Tert-Butanol-6H	0.57	1.09	64.41	0.40
Tert-Butanol-12H	0.54	1.21	68.20	0.45
Tert-Butanol-24H	0.58	1.15	65.49	0.43
Tert-Butanol-Acetonitrile-6H	0.56	0.93	62.77	0.32
Tert-Butanol-Acetonitrile-12H	0.54	1.00	66.14	0.36
Tert-Butanol-Acetonitrile-24H	0.57	0.96	62.83	0.34

limited electron diffusion by reducing the number of electrons transferred and injected, which decreased cell efficiency.

4. Conclusions

We examined the effect of solvents on the extraction of anthocyanins from blueberry and the performance of DSSCs with the dyes extracted in different solvents and for different extraction times. The light absorption spectra of TiO_2 films and the IPCE of DSSCs were measured to obtain performance data and investigate the influence of the type of solvent and extraction time on DSSC performance. The results revealed that the DSSCs with the dye extracted in tert-butanol demonstrated the best performance, whereas those with the dye extracted in acetone exhibited the worst performance. Such a result was attributed to acetone's high volatility and corresponding low reactivity with anthocyanins. The IPCE measurement results indicated that the DSSC with the blueberry dye extracted for 12 h achieved a maximum IPCE of 13%. Such results reveal that dye including anthocyanins from blueberry can be used for the fabrication of DSSCs if it is extracted with an appropriate solvent (tert-butanol in this study) and extraction time (12 h in this study). DSSCs prepared with blueberry dye using tert-butanol showed a cell efficiency of 0.45% and a fill factor of 68.20%. The extraction of anthocyanins in tert-butanol for 12 h proved to be the most appropriate extraction method for the fabrication of DSSCs. Future studies of the dye from blueberry may result in further enhancement of the overall performance of DSSCs.

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