

## Areca catechu as photovoltaic sensitizer for dye-sensitized solar cell (DSSC)

Asmaa Soheil Najm<sup>1</sup> , Hazim Moria<sup>2,\*</sup> , Norasikin Ahmad Ludin<sup>3</sup> <sup>1</sup>Department of Electrical Electronic & Systems Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia<sup>2</sup>Department of Mechanical Engineering Technology, Yanbu Industrial College, Yanbu Al-Sinaiyah 41912, Kingdom of Saudi Arabia<sup>3</sup>Solar Energy Research Institute (SERI), Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia\*corresponding author e-mail address: [moriah@rcyci.edu.sa](mailto:moriah@rcyci.edu.sa) | Scopus ID [36617578600](https://orcid.org/0009-0001-3661-7578)

## ABSTRACT

Dye-Sensitized Solar Cell (DSSC) becomes more and more interesting since a huge variety of dyes included. The natural dyes can be used as light-harvesting elements which provide the charge carriers. This contribution research on the possibility of using natural dye Areca catechu from a local Malaysian Palm tree, namely Pinang fruit, extracted by using Acetonitrile as an extracted solvent for DSSC application. This study focuses on the properties of natural dye from Areca catechu, extracted with highly acidic media. Ultraviolet-visible absorption spectroscopy (UV-Vis), Fourier Transforms Infrared (FTIR), and Photoluminescence spectroscopy (PL) have been investigated for characterized dye. The natural dye extracted from Areca catechu has interesting properties due to the high degree of molecule conjugation. This dye is capable of absorbing light quantum, at low and high energies ranging from the infrared to the Ultraviolet (UV) region. The presence of natural dye in Areca catechu crust was reported by both UV-Vis and FTIR. While the intensity of Photoluminescence emissions reported a bandgap of 1.85 eV. Areca catechu as a natural dye for DSSC sensitization, promising to achieve high cell performance, low-cost production, and non-toxicity for future applications in dye-sensitized solar cell devices.

**Keywords:** Natural Dye; Areca catechu; Dye-Sensitized Solar Cell; Acetonitrile, FTIR; Photoluminescence spectroscopy.

## 1. INTRODUCTION

Nowadays, attention is tending to renewable, sustainable energy to reduce energy consumption and environmental pollution [1]. Dye-sensitized solar cells (DSSCs) are the third generation of solar cells that possess a low cost of materials and fabrication process compared to silicon-based solar cells added with reasonable efficiency ( $\eta$ ) [2].

Nanoporous metal oxide of titanium dioxide ( $\text{TiO}_2$ ) was introduced in DSSCs by M. Gratzel and made the breakthrough in  $\eta$  of DSSCs with a value of 10% at AM 1.5 solar radiation [3]. The Gratzel's cell was composed of nanocrystalline colloidal  $\text{TiO}_2$  films sensitized by polypyridyl complexes of Ruthenium (Ru) known as the  $\text{N}_3$  dye and  $\text{I}^-/\text{I}_3^-$  solution in a volatile organic solvent as an electrolyte. In DSSC, the dye is essential in harvesting and converting photons into electrical energy; Therefore, the operation of DSSC and the performance of fabricated cell mainly depends on the type of dye sensitizer, where the adherence of the dye to the surface of semiconductor  $\text{TiO}_2$  and the absorption spectrum of the dye are essential parameters in determining the efficiency of the cell [4-5].

However, the cost of the ruthenium dye is high, along with problems in stability and efficiency, making DSSC commercialization difficult [6].

Due to this problem, the researcher searched other ways to substitute the Ru-based dye and lead to the findings in the application of organic dyes and natural dyes into DSSC. Organic dyes are economically and the highest  $\eta$  reported by using this kind of sensitizers as high as 11.9% [7]. Due to the fact that natural dyes can often inhibit the growth of microorganisms without toxicity [8]. Using plant waste to extract color and utilize for the dyeing of new natural dye is a kind of recycling that is not

only helping the environment but also promotes nature. Plants have been identified as the main sources of natural dyes. However, the extraction of natural dyes from plants sources presents challenges such as conservation. There are no specific methods for their extraction; it could depend on the goal.

Another significant problem is related to the availability of the dye source as most of the plant sources are seasonal [9]. On the other hand, natural dyes are less stable (i.e., they degrade quickly) and then cannot be kept for a long time. In nature, flowers, leaves, and fruits have different colors and contain several pigments that can be readily extracted and used for DSSC fabrication. The electronic structure of pigments reacts with sunlight to change the wavelengths. The specific color depends on the capacities of the viewer. Pigments can be described by the maximum absorption wavelength ( $\lambda_{\text{max}}$ ).

Thus, this study aims to identify a new natural dye from the local Malaysian species and investigate the possibility of its potential as a natural sensitizer with simple method extraction. Areca catechu fruit is also known to have an active carboxyl group. This paper highlights the optimum extraction method to produce the natural dye-based on Acetonitrile as a solvent. The fruit extract was characterized by UV-Vis spectrophotometer to observe the absorption spectra [10].

FTIR spectral analysis was used to determine the functional group in the nature dye [11]. Photoluminescence spectroscopy to investigate the energy levels of materials in providing fundamental information on the electronic properties and impurity levels of these materials [12]. The prospect of this cheap and new natural organic dye in DSSCs was discussed.

## 2. MATERIALS AND METHODS

Malaysian Pinang fruit used to extract the new natural dye. Generally, this palm species of *Areca catechu* grows in the tropical regions of Asia and parts of East Africa [13] and locally called the Betel tree. The seed contains alkaloids such as arecaidine and arecoline. The sliced seeds (endosperm) are chewed as a mild stimulant, sometimes together with other leaves such as pepper plants or Gambier. *Areca catechu* has antidepressant properties in rodents [14], [15], and it largely contains sugars, lipids, as well as polyphenols [16]. Polyphenols are the most bioactive components in *Areca catechu*, which comprised of condensed tannins, hydrolysable tannins, and flavonols. Figure 1 displays the chemical structure of catechins present in *Areca catechu*.

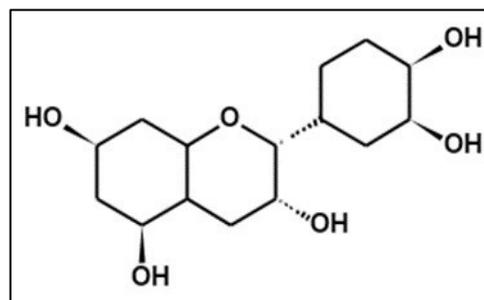


Figure 1. Chemical structure of catechin contained in *Areca catechu*.

## 3. RESULTS

### 3.1. Acetonitrile as a solvent.

Solvents can have an effect on solubility, stability, and reaction rates and choosing the appropriate solvent for extraction. Table 1 shows the main physical properties for traditional solvents used in extraction.

Table 1. Physical properties of some common organic solvents\*.

Solvents	Formula	Boiling Point (°C)	Viscosity (cP 25°C)	Polarity	Solubility in Water (g/100 g)
Hexane	C <sub>6</sub> H <sub>14</sub>	69	0.31	0.1	0.0014
Acetone	C <sub>3</sub> H <sub>6</sub> O	56.2	0.31	5.1	M
Acetonitrile	C <sub>2</sub> H <sub>3</sub> N	82	0.33	5.8	M
Chloroform	CHCl <sub>3</sub>	61.2	0.54	4.1	0.8
Ethanol	C <sub>2</sub> H <sub>6</sub> O	78.5	1.07	5.2	M
Toluene	C <sub>7</sub> H <sub>8</sub>	110.6	0.56	2.4	0.05
Methanol	CH <sub>4</sub> O	64.6	0.54	5.1	M
Ethyl ether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	34.6	0.224	2.8	6.05
Pyridine	C <sub>5</sub> H <sub>5</sub> N	115	0.88	5.3	M

\*The values were sourced from online and hardbound compilations. Relative polarity data: [17], M: completely miscible.

The high popularity of acetonitrile is due to its excellent solvation ability with respect to a wide range of polar and nonpolar solutes, and favourable properties such as low freezing/boiling points, low viscosity, and relatively low toxicity [18]. Acetonitrile is a common two-carbon building block in organic molecules to construct many useful chemicals, including acetamide hydrochloride, thiamine, and  $\alpha$ -naphthalene acetic acid, and also one of the key reasons for this is that it contains a hydrophobic methyl group connected to a hydrophilic cyano group [19], Figure 2.

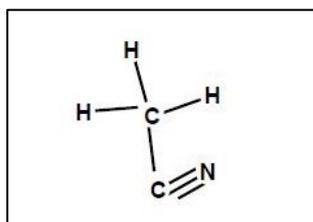


Figure 2. Chemical structure of Acetonitrile.

### 3.2. Preparation of sensitizer.

Following the protocol used in the earlier work [20-21], the natural dye was prepared. Fruits crust of *A. catechu* plant was

taken and washed using distilled water. Then, it was dried under diffused solar radiation by keeping in the open room atmosphere for 2-3 days before being crushed into a fine powder using a grinder (Mulry function disintegrator SY-04). Next, about 40 g of the resultant powder was immersed in 100 mL of acetonitrile (Sigma-Aldrich). Later, the obtained solutions were placed in a shaker (Ambient Shaker Incubators, SKU: SI-100) for 24 hours. Finally, the extract was separated using filter paper (NICE, 12.5 cm, 102 Qualitative) to achieve a clear dye solution.

### 3.3. Characterization.

The absorption spectra of freshly prepared *Areca catechu* dye were determined using Ultraviolet-Visible spectroscopy (Perkin Elmer, Lambda 35) in the range of 200 nm to 900 nm. Meanwhile, the chemical structure of the *Areca Catechu* dye solution was examined by FTIR technique (Model NICOLET 6700 FT-IR), in the range of 4000-400 cm<sup>-1</sup>. Photoluminescence (PL) spectra were recorded using a fluorescence spectrometer 50560.

### 3.4. Results and discussion.

Note that as a general principle, focus in this paper on the effect of solvent by UV-Vis, and the chemical structure for the natural dye from FTIR and the bandgap effective from PL analysis.

#### 3.4.1. Effects of Solvent on the Absorbance of Extracted Natural Dye.

The natural dye extracted from *Areca catechu* in Acetonitrile solvent showed a light yellow color. This dye solution revealed a strong absorption band (Figure 3) in the UV-Vis wavelength region that occurred from 350 nm to 512 nm, which is located within visible range and refers to violet color, which is considered as the highest frequency color. The absorption spectra of the dye were depended on the chemical structure and the polarity of the dye.

#### 3.4.2. Fourier Transform Infrared Spectroscopy (FTIR).

The Fourier Transform Infra-Red spectra of *Areca catechu* is shown in Figure 4 explained how the solvent can express the characterization of a functional group for natural dye. In this study, four possible coordination environments were identified [22]. First structures indicated that spectra have the characteristic vibration of (O – H) stretch at 2937.01, 2262.59, cm<sup>-1</sup>, consider as a carboxylic acid group. The second absorption peaks at 1448.64, 1370.15 cm<sup>-1</sup> is assigned for (H – C – H) bending modes. The third functional group (O – C) appears at 1041.66 cm<sup>-1</sup>. While fourth is related to (C – O – C) stretching bands 912.79 and 750.96

$\text{cm}^{-1}$  that are typical of aromatic molecules. The last absorption peaks between  $3000\text{ cm}^{-1}$  and  $3700\text{ cm}^{-1}$  are assigned to (O – H) stretching vibration mode of water molecules. The interaction behavior of the components can be observed through the identification of the changes in the FTIR spectral features for intensity, bandwidth, and position.

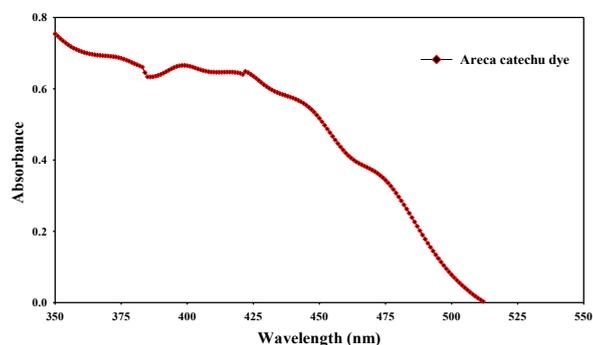


Figure 3. UV-Vis spectra of Areca catechu dye.

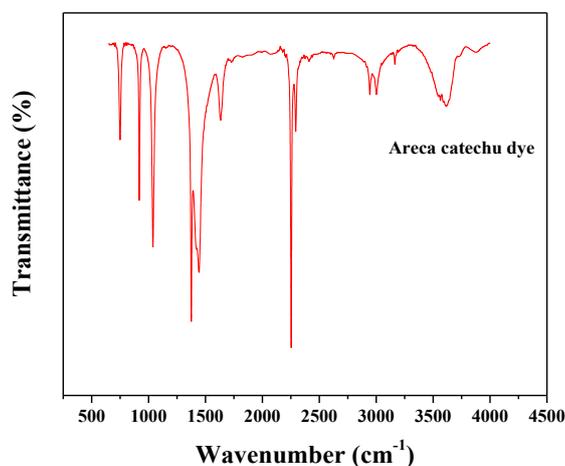


Figure 4. FTIR Spectra of Areca catechu dye.

### 3.4.3. Photoluminescence Spectroscopy (PL).

Photoluminescence Spectroscopy (PL) is a suitable tool to study the efficiency of charge carrier trapping, migration, and

## 4. CONCLUSIONS

A new natural dye extracted from Pinang Palm (Areca catechu) was successfully used as a dye sensitizer based DSSC. The objective was to investigate the extract under Acetonitrile solvent and study characterization with optical properties as a sensitizer for dye-sensitized solar cells. Areca catechu was successfully characterized by UV-Vis, FTIR, and PL in order to investigate its characterization. It promised strong interaction with the  $\text{TiO}_2$  surface and photosensitization because of the hydroxyl and carboxylic functional groups. The UV-Vis measurement proved the high absorbance of Areca catechu. The obtained results represent a significant step forward in defining the structure of Areca catechu dye and may prove of great interest in the production of semiconductor materials and in potential uses of

## 5. REFERENCES

- Patil, D.; Jadhav, M.; Avhad, K.; Chowdhury, T.H.; Islam, A.; Bedja, I.; Sekar, N. A new class of triphenylamine-based novel sensitizers for DSSCs: a comparative study of three

transfer, and to understand the fate of electron-hole pairs in semiconductor particles because PL emissions result from the recombination of free carriers [23]. Areca catechu dye will absorb the incident photons with sufficient energy equal to or higher than the band-gap energy, which will produce photo-induced charge carriers ( $h^+ \dots e^-$ ). In addition, the recombination of photo induced electrons and holes releases energy in the form of PL emission spectra. Hence, a higher PL intensity indicates less charge recombination. The band gap energy can be calculated using the relation,  $E_g = 1242 / \lambda$ , eV with  $\lambda$  in nm [24]. Figure 5 shows Photoluminescence spectra of Areca catechu dye with wavelengths recorded 672 nm.

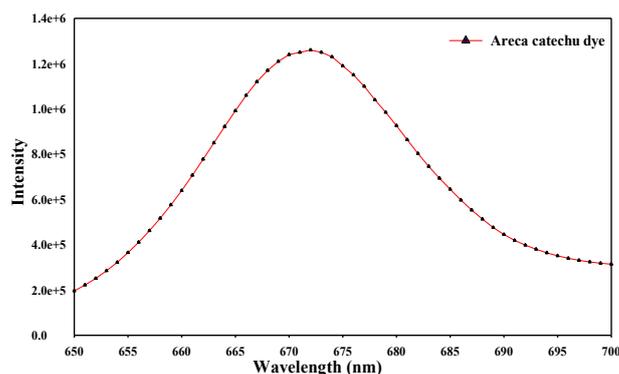


Figure 5. Photoluminescence spectra of Areca catechu dye.

Table 2. Characterizations for Areca catechu dye

Criterion	Areca catechu dye
Wavelength (nm)	448
Absorbent (a.u)	0.408
Carboxyle group ( $\text{cm}^{-1}$ )	2944.44, 2293.70, 1634.81, 1443.28, 1375.65, 1039.02
Band Gap (ev)	1.848

Areca catechu dye exhibits a bandgap of 1.848 eV. The smaller bandgap led to a large photocurrent because of the utilization of the long-wavelength region in the solar spectrum. Table 2 indicates the summary of the absorbance and Chemical Structure obtain for Areca catechu dye.

Areca catechu as photovoltaic cells especially DSSC. These results clearly show that Areca catechu can be applied as a natural dye to DSSC. It is promising for the realization of high cell performance, low-cost production, and non-toxicity. It should be emphasized here that natural dyes from food are better for human health than synthetic dyes. Advances in the novel nature-inspired sensitizers can result in reducing the cost of production and improving the stability of the dye. Industrial interest in organic photovoltaic technology is high at the moment, and that will cause continued investment. However, there is an agreement that these problems will be resolved as the technology matures, or at least problems will be mitigated.

different anchoring groups. *New Journal of Chemistry* **2018**, *42*, 11555-11564, <https://doi.org/10.1039/C8NJ01029C>.

2. Tathavadekar, M.; Biswal, M.; Agarkar, S.; Giribabu, L.; Ogale, S. Electronically and Catalytically Functional Carbon

Cloth as a Permeable and Flexible Counter Electrode for Dye Sensitized Solar Cell. *Electrochimica Acta* **2014**, *123*, 248-253, <https://doi.org/10.1016/j.electacta.2013.12.175>.

3. Graetzel, M. Dye-Sensitized Solar Cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2003**, *4*, 145-153, [https://doi.org/10.1016/S1389-5567\(03\)00026-1](https://doi.org/10.1016/S1389-5567(03)00026-1).

4. Al-Alwani, M.A.M.; Mohamad, A.B.; Ludin, N.A.; Kadhum, A.A.H.; Sopian, K. Dye-sensitized solar cells: Development, structure, operation principles, electron kinetics, characterisation, synthesis materials and natural photosensitizers. *Renewable and Sustainable Energy Reviews* **2016**, *65*, 183-213, <https://doi.org/10.1016/j.rser.2016.06.045>.

5. Faris Abdullah, M.; Zulkifli, R.; Harun, Z.; Abdullah, S.; Wan Ghopa, W.A.; Soheil Najm, A.; Humam Sulaiman, N. Impact of the TiO<sub>2</sub> Nanosolution Concentration on Heat Transfer Enhancement of the Twin Impingement Jet of a Heated Aluminum Plate. *Micromachines (Basel)* **2019**, *10*, 176, <https://doi.org/10.3390/mi10030176>.

6. Wongcharee, K.; Meeyoo, V.; Chavadej, S. Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers. *Solar Energy Materials and Solar Cells* **2007**, *91*, 566-571, <https://doi.org/10.1016/j.solmat.2006.11.005>.

7. Green, M.A.; Dunlop, E.D.; Levi, D.H.; Hohl-Ebinger, J.; Yoshita, M.; Ho-Baillie, A.W.Y. Solar cell efficiency tables (version 54). *Progress in Photovoltaics: Research and Applications* **2019**, *27*, 565-575, <https://doi.org/10.1002/ppp.3171>.

8. Han, S.; Yang, Y. Antimicrobial activity of wool fabric treated with curcumin. *Dyes and Pigments* **2005**, *64*, 157-161, <https://doi.org/10.1016/j.dyepig.2004.05.008>.

9. Zongo, S. Nonlinear optical properties of natural dyes based on optical resonance. PhD diss., University of the Western Cape, 2012.

10. Pomeranz, Y.; Clifton, E.M. Enzymatic methods. In: *Food Analysis*. Springer, Boston, MA, 1994; pp. 506-531.

11. Centeno, S.A.; Shamir, J. Surface enhanced Raman scattering (SERS) and FTIR characterization of the sepia melanin pigment used in works of art. *Journal of Molecular Structure* **2008**, *873*, 149-159, <https://doi.org/10.1016/j.molstruc.2007.03.026>.

12. Gfroerer, T.H. Photoluminescence in analysis of surfaces and interfaces. In: *Encyclopedia of analytical chemistry: applications, theory and instrumentation*. 2006; <https://doi.org/10.1002/9780470027318.a2510>.

13. Heatubun, C.; Dransfield, J.; Flynn, T.; Tjitrosodirdjo, S.; Moge, J.; Baker, W. A monograph of the betel nut palms (Areca: Arecaceae) of East Malesia. *Botanical Journal of the Linnean Society* **2012**, *168*, 147-173, <https://doi.org/10.1111/j.1095-8339.2011.01199.x>.

14. Shrestha, J.; Shanbhag, T.; Shenoy, S.; A muthan, A.; Prabhu, K.; Sharma, S.; Banerjee, S.; Kafle, S. Antioviulatory and abortifacient effects of Areca catechu (betel nut) in female rats. *Indian journal of pharmacology* **2010**, *42*, 306-311, <https://doi.org/10.4103/0253-7613.70350>.

15. Amarasinghe, H.K.; Usgodaarachchi, U.S.; Johnson, N.W.; Lalloo, R.; Warnakulasuriya, S. Betel-quid chewing with or without tobacco is a major risk factor for oral potentially malignant disorders in Sri Lanka: a case-control study. *Oral oncology* **2010**, *46*, 297-301, <https://doi.org/10.1016/j.oraloncology.2010.01.017>.

16. Jung, J.S. Making of Natural Dyeing Scarves by Tie-Dyeing Technique. In: *MATEC Web of Conferences*. EDP Sciences, Volume 108, 2017; pp. 03006.

17. Dong, T.; Knoshaug, E.P.; Pienkos, P.T.; Laurens, L.M.L. Lipid recovery from wet oleaginous microbial biomass for biofuel production: A critical review. *Applied Energy* **2016**, *177*, 879-895, <https://doi.org/10.1016/j.apenergy.2016.06.002>.

18. Ian, F.; Woods, D.; Lewis, M.; Gan, Q.; Nancarrow, P. The Importance of Acetonitrile in the Pharmaceutical Industry and Opportunities for its Recovery from Waste. *Organic Process Research & Development* **2012**, *16*, 612-624, <https://doi.org/10.1021/op2003503>.

19. Wang, S.Y.; Xue-Qiang, C.; Yi, F.; Shun-Jun, J. Acetonitrile as Reagents in Organic Synthesis: Reactions and Applications. In: *Solvents as Reagents in Organic Synthesis: Reactions and Applications* 355-375, 2017.

20. Soheil, A.; Mohamad, A.B.; Ludin, N. *The extraction and absorption study of natural dye from Areca catechu for dye sensitized solar cell application*. Volume 1838, 2017; pp. 020019.

21. Soheil, A.; Ludin, N.; Faris, M.; Almessiere, M.; Alrawi, N.; Al-Alwani, M. Areca catechu extracted natural new sensitizer for dye-sensitized solar cell: performance evaluation. *Journal of Materials Science: Materials in Electronics* **2020**, *31*, <https://doi.org/10.1007/s10854-020-02905-x>.

22. Narain, R. *Engineered carbohydrate-based materials for biomedical applications: polymers, surfaces, dendrimers, nanoparticles, and hydrogels*. John Wiley & Sons; Hoboken, New Jersey. Published simultaneously in Canada. 2011.

23. Chang, J.; Xiao, J.; Lin, Z.; Zhu, H.; Xu, Q.-H.; Zeng, K.; Hao, Y.; Ouyang, J. Elucidating the charge carrier transport and extraction in planar heterojunction perovskite solar cells by Kelvin probe force microscopy. *Journal of Materials Chemistry A* **2016**, *4*, 17464-17472, <https://doi.org/10.1039/C6TA05350E>.

24. Mir, N.; Salavati-Niasari, M. Photovoltaic properties of corresponding dye sensitized solar cells: Effect of active sites of growth controller on TiO<sub>2</sub> nanostructures. *Solar Energy* **2012**, *86*, 3397-3404, <https://doi.org/10.1016/j.solener.2012.08.016>.

## 6. ACKNOWLEDGEMENTS

The authors owe heartfelt thanks to the Solar Energy Research Institute in Universiti Kebangsaan Malaysia and Yanbu Industrial College for their support in this research.



© 2020 by the authors. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).