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Research Article

Active carbon derived from rice husk as sustainable substitutes for costly platinum electrodes in dye-sensitized solar cells



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ABSTRACT

Significant financial and environmental challenges are associated with using platinum electrodes as counter electrodes (CEs) in dye-sensitized solar cells (DSCs). This work uses rice husk, an agricultural waste, to create active carbon that is appropriate for DSC CEs in response to these difficulties. A simple spray pyrolysis technique created activated carbon obtained from rice husks. The DSC employing activated rice husk carbon as the CE demonstrated a conversion efficiency of 6.06%, slightly lower than the 8.21% efficiency achieved with a platinum electrode-based cell. However, this performance gap is overshadowed by the substantial cost reduction enabled by the utilization of low-cost activated carbon compared to noble metal alternatives. This result introduces promising avenues for investigating the use of agriculturally derived carbon materials as workable and affordable options for platinum CEs in DSCs, thereby contributing to the sustainable advancement of photovoltaic systems. Even though the performance of DSC that uses activated carbon derived from rice husk in CE is slightly lower than its counterparts based on platinum, the cost reduction due to the use of low-cost activated carbon with noble metal is significant.

alternative CEs.

Considering the above facts, several ranges of carbonaceous materials such as carbon nanotubes, Graphene [4,5], Graphite [6,7], carbon black [8], Activated carbon [3,9,10], etc have been investigated to make effective CEs for DSCs. Among them, activated carbons (ACs) are easily available, and low cost, and the preparation method from biomass is simple and environmentally friendly compared to other carbon materials. AC is a carbonaceous material made from many different kinds of carbon-rich materials, such as coal and wood. AC is normally produced in two phases, with raw materials being carbonized at relatively low temperatures and then activated at high temperatures. To lower the production costs and conserve the environment, various agricultural wastes including rice husk, coconut shells, and empty fruit bunches were reported as raw materials for the production of AC.

Rice husk, the outer layer of rice grains is a mass-scale agricultural biomass waste product available in rice-producing regions, making it a more environmentally friendly and low-cost option. Furthermore, activated rice husk carbon (ARHC) has a high porosity which yields a high surface area [9,10]. Although ACs are made from biological materials have lower electronic conductivities than graphene, carbon black, and carbon nano-tubes. Despite this, they offer a compelling solution due to their abundance and cost-effectiveness.

Recent advancements in DSC technology have seen a surge in the application of biomass-derived carbon materials as alternative CEs. These materials hold significant promise in addressing the cost and sustainability challenges associated with traditional Pt-based CEs. In this present work, our main objective was to investigate the possibility of preparing low-cost Pt-free DSCs with high energy conversion efficiency by preparing CEs using AC derived from rice husk. By exploring the properties and performance of AC in comparison to platinum, we aimed to gain insights into the feasibility and effectiveness of using activated rice husk carbon as a sustainable and cost-effective alternative in DSCs.

2. Experimental

2.1. Preparation of activated rice husk carbon powder

Electrically conductive porous activated rice husk carbon (ARHC) was prepared from the outer shell of rice grains which is agricultural biomass waste in Sri Lanka. As shown in Fig. 1 the Rice husk (RH) was

cleaned using distilled water to remove dust and other impurities. Then washed RH was dried using a hot plate. Typically, 25 g of dried rice husk was treated with 500 ml of 1 M NaOH solution for 24 h at room temperature before being dried in an oven for another 24 h to remove silica from RH. Then treated RH was carbonized in a box furnace at 400 °C for 30 min to produce the rice husk charcoal (RHC). This RHC was dipped in 300 ml of 1 M NaOH solution at room temperature for 24 h to remove any trace of silica to obtain a pure form of RHC. Then the RHC was washed again with copious amounts of distilled water to eliminate any residual NaOH, as confirmed by pH measurement before being filtered and dried. For the activation process, the cleaned RHC was heated at 900 °C for 20 min in a box furnace, and the hot RHC was dropped instantly into the distilled water tank for quenching and dried using a hot plate. Then dried ARHC was ground into a powder using a disk mill machine. The produced ARHC powder was characterized by XRD (Rigaku Ultima IV X-ray Diffractometer equipped with a Cu anode and dual detectors), Raman spectroscopy (Renishaw Invia Reflex Raman microscope), Brunauer-Emmett-Teller (BET) surface area analysis, and FT-IR (Bruker Alpha FT-IR spectrometer). The pore volume of the product was taken using the Horvath-Kawazoe Method (HK).

2.2. Preparation of TiO₂ working electrode

The TiO₂ working electrode was prepared as reported in previous work [11]. Fluorine-doped tin oxide (FTO) glass substrates were initially cleaned using detergent in an ultrasonicator for 15 min, followed by thorough rinsing with distilled water and isopropanol, and then left to air-dry. To prepare the TiO₂ colloidal solution, 8.0 ml of Titanium tetraisopropoxide and 8.0 ml of absolute ethanol were mixed with acetic acid (1.0 ml) and steam was passed through the solution to aid rapid hydrolysis. When the solution was exposed to steam it produced a transparent solid mass consisting of TiO₂ nanoparticles. The transparent solid was ground with 20.0 ml of distilled water in a mortar and sonicated for 10 min. The dispersion was then sterilized in an autoclave at 150 °C for 3 h. The prepared TiO₂ colloidal solution (30.0 ml), acetic acid (8.25 ml), Triton X-100 (8 drops), and 30 ml of absolute ethanol were mixed and grounded using a mortar and pestle. Finally, the TiO₂ suspension was sonicated for 10 min. The precursor solution was sprayed onto pre-heated (150 °C) cleaned FTO glass substrates. TiO₂ film has a thickness of around 10 µm, prepared using the above manner.

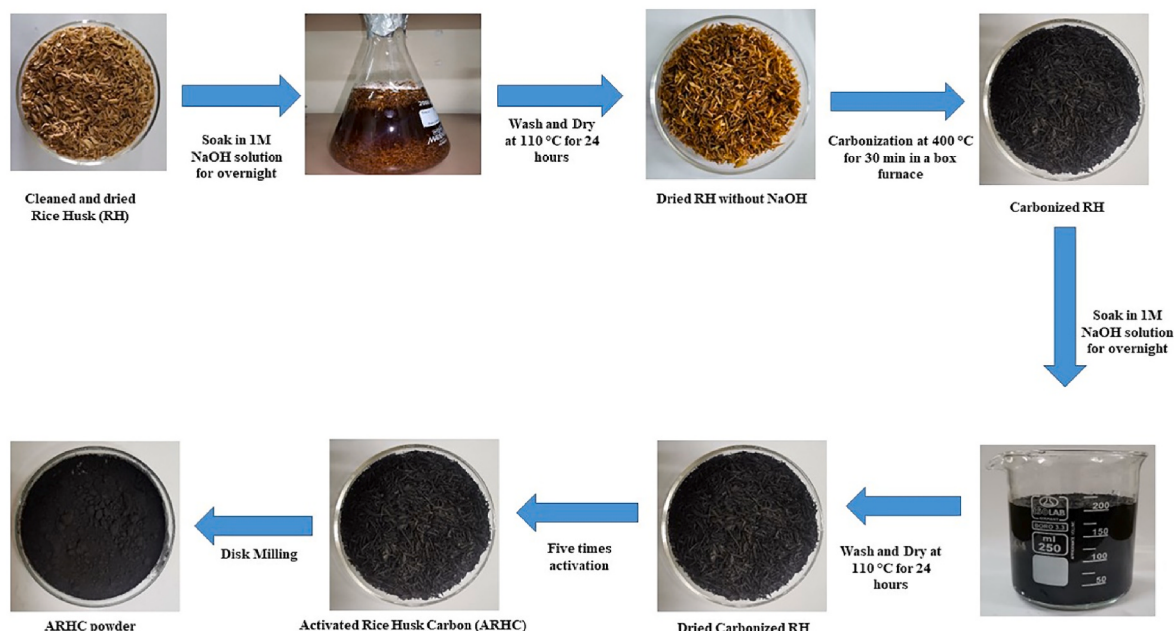


Fig. 1. Schematic diagram of the steps involved in producing activated rice husk carbon powder.

Then sprayed TiO₂ plates were sintered at 500 °C for 30 min in air, cooled to 80 °C and immersed overnight in a 0.3 mM solution of Ruthenium-based N719 dye.

2.3. Preparation of activated rice husk carbon-coated counter electrode

The suspensions of ARHC were prepared using 0.5 g of ARHC powder, 10.0 ml of isopropanol, and different amounts (from 0.04 g to 0.10 g increased by 0.01 g at a time) of polyvinylpyrrolidone (PVP) binder, sprayed onto cleaned FTO substrates at different temperatures from 50 °C to 250 °C and sintered at 300 °C for 20 min in a box furnace. Then films were characterized by Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX). The electrical conductivity of ARHC was measured by the four-probe method. To explore the electrocatalytic characteristics of the ARHC CE, cyclic voltammetry (CV) experiments were conducted employing a three-electrode setup, with an Ag/AgCl reference electrode, Pt wire serving as the counter electrode, and either Pt or ARHC-CE as the working electrode. The investigations were carried out at a scan rate of 30 mV s⁻¹. A diluted electrolyte solution composed of acetonitrile, with a mixture of 10 mM LiI, 1 mM I₂, and 0.1 M LiClO₄, was utilized for the experiments.

2.4. Construction of DSC

The activated rice husk carbon (ARHC) or Pt counter electrodes were gently clipped onto the dye-coated photoanode. The space between the two electrodes was filled with a liquid electrolyte containing 0.6 M dimethylpropyl imidazolium iodide, 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. A mask with a window size of 0.25 cm² was placed on the photoanode, and the solar cell characteristics were evaluated using a simulated sunlight source, specifically the SPD SS-25 LED Solar Simulator (AM 1.5 AT 100 mW/cm²), and a VK-PA-300 K PV power analyzer. The incident photon-to-current efficiency (IPCE) spectrum was recorded using the Bentham TMC300 monochromator for both the activated rice husk carbon and platinum CEs. Also, the impedance measurements were taken using Metrohm Autolab Potentiostat/Galvanostat Electrochemical Analyzer covering the frequency range from 10⁻² to 10⁶ Hz.

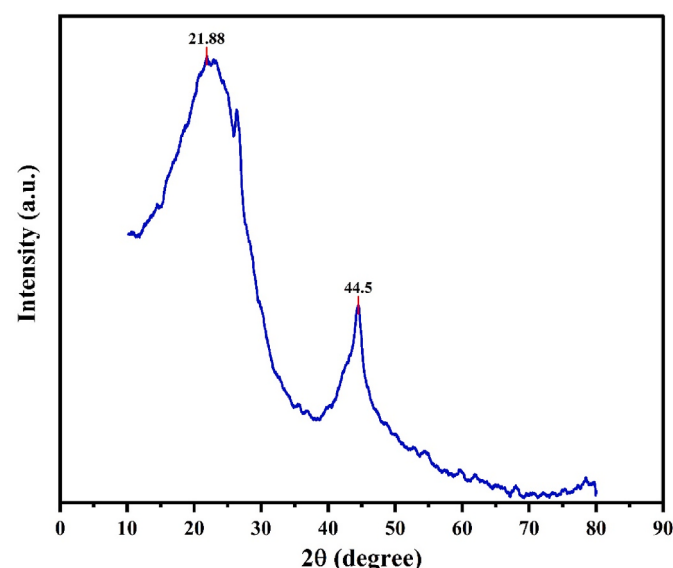


Fig. 2. X-ray diffractogram of activated rice husk carbon.

3. Results and discussion

3.1. Crystallography of ARHC

The X-ray diffractogram (XRD) of the prepared ARHC is shown in Fig. 2 and the respective lattice spacing (*d*), full-width half maximum (FWHM), and crystalline and crystal planes respective to the XRD peaks determined by analyzing XRD spectra are given in Table 1 and the corresponding standard JCPDS Card number of ARHC is 75–1621. As seen in Fig. 2, ARHC exhibited two low intensities and broad and weak diffraction peaks. XRD patterns show the broad peak at around 22° is assigned to the amorphous silica [12–15]. The other weak broad peak at about 44° corresponds to the (100) carbon plane, indicating the formation of a low crystallinity degree of amorphous carbon [16]. Another diffraction peak at around 26° indicated overlapping peaks of the (200) plane of amorphous carbon and amorphous silica, and Rong et al. have reported somewhat similar XRD results for rice husk-based activated carbon [16].

3.2. Raman spectroscopy of ARHC

The structure of the ARHC was further studied using Raman spectroscopy (Fig. 3). Two noticeable peaks were observed at 1349 cm⁻¹ and 1596 cm⁻¹ which correspond to the D band and G bands respectively. The D band at about 1349 cm⁻¹ is attributed to the disordered carbonaceous structure of the activated rice husk carbon. Hence, it is known that the D band represents the defects of the carbonaceous structure. Furthermore, the G band (1596 cm⁻¹) is due to the presence of C=C stretching vibrations in the ARHC sample [17,18]. The R-value was calculated using *I*_D and *I*_G values by the following equation.

$$R = \frac{I_D}{I_G} \quad \text{Equation 1}$$

The R-value of ARHC is about 0.92. It indicates the presence of a high percentage of structural defects in the ARHC sample, which could be due to NaOH related activation process [19]. The efficient reduction of I₃ is attributed to the presence of structural defects and disorder, as indicated by Raman spectroscopy studies that show a higher number of edges in the ARHC sample. This characteristic makes an obvious advantage for the performance of activated carbon derived from rice husk CEs. Therefore, these results suggest that ARHC is good for application as CEs in DSCs. Also, according to the BET surface area analysis, the BET surface area and the pore volume of the ARHC powder are 875.38 m²/g and 0.42 cm³/g respectively.

3.3. FT-IR spectrum analysis of ARHC

Fig. 4 shows the FT-IR spectrum of the prepared ARHC powder. The absence of the wide band at around 3420 cm⁻¹ indicated that the sample didn't consist of absorbed water of O–H hydroxyl bonds. This can happen due to the removal of moisture during the activation process. The bands at around 2362 cm⁻¹ and 2344 cm⁻¹ are attributed to C≡C stretching vibrations. Also, the peak at 1557.7 cm⁻¹ is due to the aromatic C=C bond [20]. The highly intense band at 1557.7 cm⁻¹ is related to stretching vibrations of C–O in esters, alcohol, or phenol groups. In

Table 1

Data extracted from XRD is shown in Fig. 2.

Peak positions 2θ/degree	Lattice spacing <i>d</i> /Å	FWHM	Crystallite size/nm	Material	Orientation
21.8	4.28	18.31	44	Amorphous silica	002
44.5	2.03	9.17	93	Amorphous carbon	100

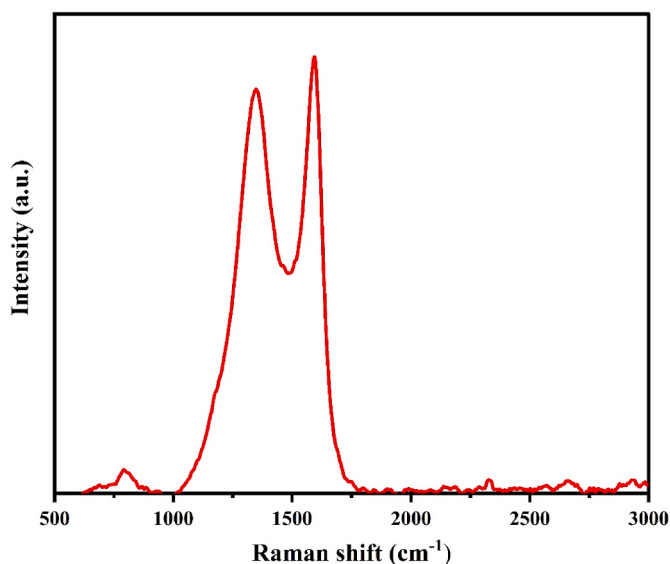


Fig. 3. The Raman spectrum of the ARHC.

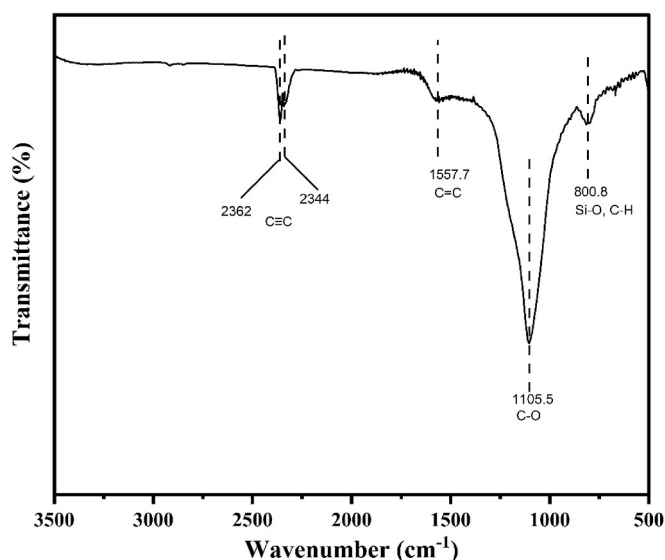


Fig. 4. FT-IR spectrum of the prepared ARHC.

addition, a significant peak that appeared at around 750–875 cm^{-1} is attributed to silica bond or aromatic C–H out-of-plane bending vibration. Normally, a peak around 798 cm^{-1} shows the stretching vibrations of the silica bond [21,22].

3.4. Electrical properties of CEs

In order to fabricate appropriate CE electrical properties were analyzed by varying the FTO substrate temperature during the spraying.

Table 2

Variation of sheet resistance and electrical conductivity with the temperature of the substrate during the spraying.

Spray substrate temperature/ $^{\circ}\text{C}$	$R_{\text{sh}}/\text{k}\Omega$ sq^{-1}	Resistivity (ρ)/ $\text{m}\Omega$ cm	Conductivity (σ)/ kS m^{-1}
50	33.3	39.37	2.54
100	8.1	7.52	13.30
200	20.2	20.89	4.78

The measured sheet resistance and the electrical conductivity of the film using the four-probe method are given in Table 2 as a function of substrate temperature. The ability of electrical charge to travel in the plane of the film, or the electrical conductivity of the film is given in Table 2. The lowest sheet resistance of $8.1 \text{ k}\Omega \text{ sq}^{-1}$ and conductivity of 13.30 kS m^{-1} are observed for the CEs prepared by increasing the FTO substrate temperature to 100°C . Owing to higher-charge transport better solar cell performances can be expected with the film prepared at 100°C .

3.5. Morphology and structural of CEs

The SEM images of ARHC thin film prepared on the FTO glass substrates are shown in Fig. 5. Fig. 5(a), 5(b), 5(c) reflect those prepared on heated substrates at 50°C , 100°C , and 200°C temperatures respectively. ARHC-CE produced at 50°C , 100°C , and 200°C have spongy surface morphologies, as inferred from the SEM images. All the films exhibited the formation of some pores. The pore size is gradually increasing with increasing substrate temperature. The CE prepared at 100°C has a porous nature, and as the temperature rises, more clusters develop on the surface of the FTO substrate. Because the suspension was sprayed onto the FTO substrate at high spray temperature, suspension can't spread on the substrate uniformly. When clusters form, electrons might become trapped within the clusters at boundaries hindering the charge transport and thus increasing electron recombination. In addition, the high density of small pores in Fig. 5(b) indicates the higher liquid electrolyte CE contact area of CE prepared at 100°C which enhances electron collection by triiodide in the electrolyte from the CE.

Fig. 6(a) illustrates the SEM image of ARHC film prepared at 100°C together with the EDX spectrum [Fig. 6(b)], which was taken by coating an Osmium conducting layer about 3 nm. EDX structure and elemental distribution mapping reveals atomic weight percentages of C 78.8%, O 17.3%, Na 2.7%, and less amount of Si 0.7%. These results agree with FT-IR spectrum data where functional groups such as C–C, Si–O, C–O, etc. are included in this ARHC film.

Moreover, as shown in Table 2 the pre-heated temperature of FTO substrates increased, and electrical conductivity increased after 100°C spray temperature the conductivity dropped again due to the clusters appearing on the surface as revealed in SEM images. These results can be concluded that slower electron transfer rates to the I_3^- ions at the CE are caused by the ARHC film's poor electrical conductivity at higher and lower spray temperatures except 100°C . Fig. 7 shows the cross-sectional SEM of the CEs. The average thickness of the ARHC layer on FTO can be estimated to be $23 \mu\text{m}$.

3.6. Optimization of photovoltaic performance of DSCs

3.6.1. Effect of PVP binder on counter electrode characteristics

The performance of ARHC-CE was optimized by changing the amount of the PVP binder in the CE and the FTO glass substrate temperature. The photovoltaic parameters (V_{OC} = open circuit voltage, J_{SC} = short circuit current density, FF = fill factor, η = conversion efficiency) of fabricated DSCs with ARHC CEs prepared by changing the amount of PVP binder are summarized in Table 3.

The ARHC layers prepared using less than 0.04 g of PVP binder were peeling off due to poor adhesion with the FTO substrates. As the amount of PVP increases from 0.04 g to 0.10 g the FF is gradually decreased. The attenuation observed in FF , J_{SC} reveals that the series resistance of the cell is increased and dye regeneration kinetics must have been hindered due to the sluggish reduction of I_3^- at the CE. Therefore, the efficiency of the DSCs decreases. On the other hand, these findings suggest that when the amount of PVP binder is very low, there is insufficient adhesion of the ARHC layer to the FTO substrate, leading to reduced electrical conductivity in the CEs.

3.6.2. Effect of spray temperature of the counter electrode

Table 4 shows the performance of DSCs with ARHC CEs prepared at

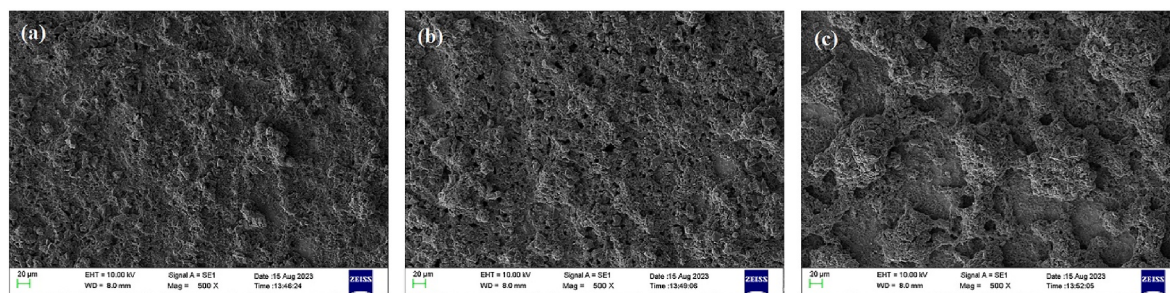


Fig. 5. SEM images of ARHC-CE prepared at (a) 50 °C (b) 100 °C and (c) 200 °C.

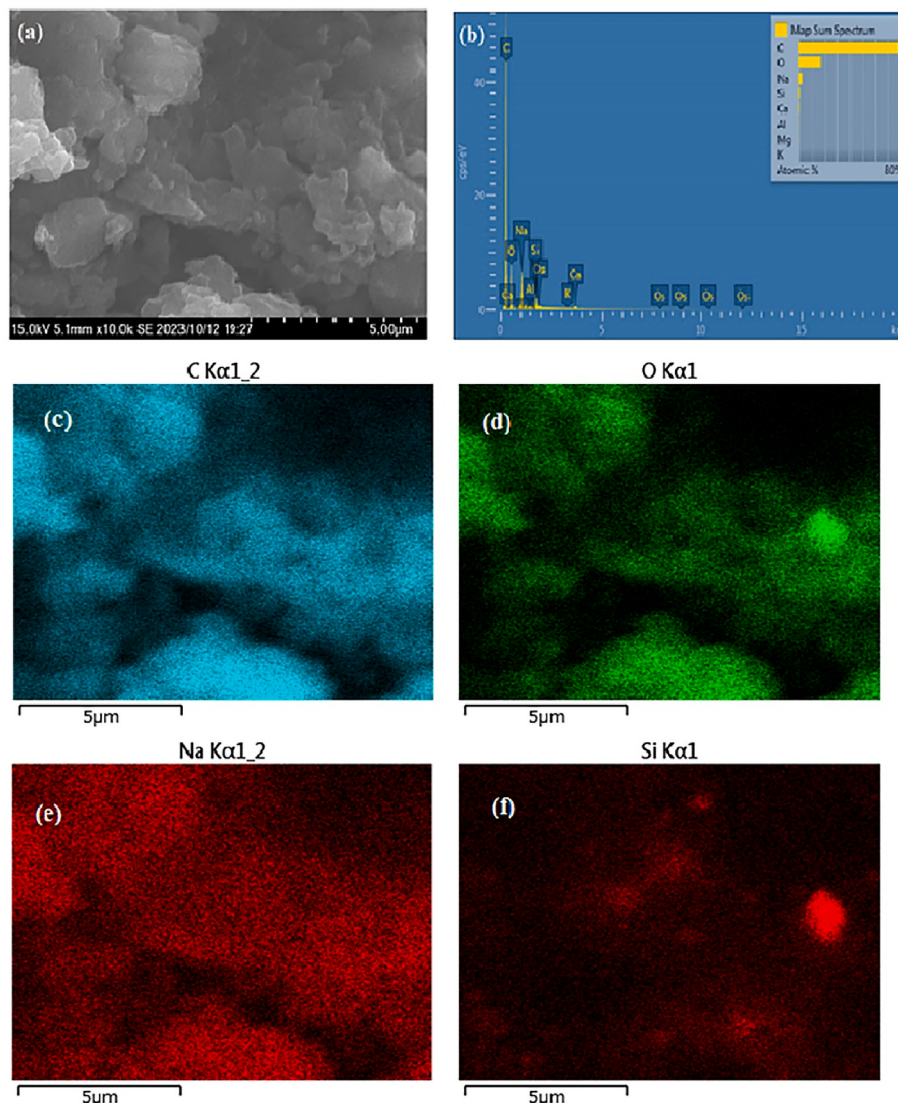


Fig. 6. (a) SEM image of activated rice husk carbon film (b) corresponding EDX spectrum, majority elemental distribution (c) Carbon (C) (d) Oxygen (O) (e) Sodium (Na) (f) Silicon (Si).

different spray temperatures. At below 100 °C temperature, a considerable amount of PVP binder is present in the CE material and it enhances the resistance of the ARHC-CE which results in low efficiency. At the adequate temperature of 100 °C, the PVP binder is burnt out to a certain extent. It provides good adhesion between ARHC particles, and the ARHC layer to the FTO substrate as revealed in the cross-sectional SEM image (Fig. 7), also which gives a low resistance value and higher performance. As the spraying temperature increases above

100 °C, sprayed ARHC suspension formed clusters on the FTO substrate as shown in Fig. 5(c) SEM image. It results in poor adhesion and higher resistance, ultimately it reduced the performance of DSCs. Also, these results agree with sheet resistance and electrical conductivity measurements in Table 2. Therefore, it can be assumed that the performance of DSCs with ARHC CEs is fundamentally reliant on the compromise between the electrical conductivity and the adhesiveness of the ARHC layer to the FTO substrate.

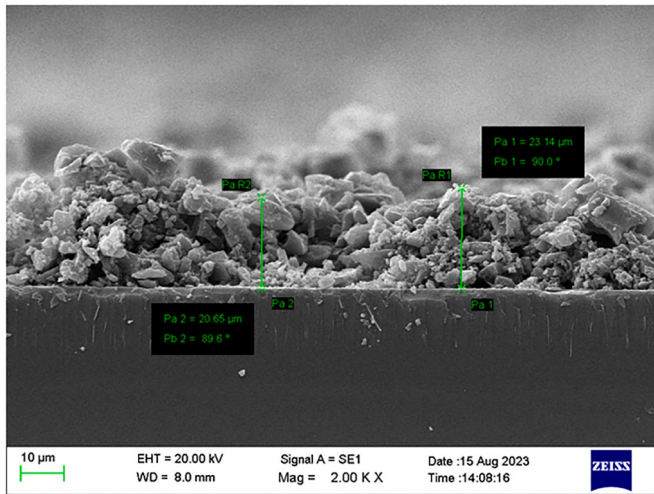


Fig. 7. Cross-sectional SEM image of ARHC layer on FTO substrate prepared using the optimized amount of PVP binder (0.06 g) and spray temperature (100 °C).

Table 3

Photovoltaic parameters of DSCs with ARHC-CE prepared by changing the PVP binder amount at a constant spray temperature of 50 °C.

PVP amount added to 0.50 g ARHC/g	V_{OC}/V	$J_{SC}/\text{mA cm}^{-2}$	FF	$\eta/\%$
0.04	0.65	10.82	0.53	3.61
0.05	0.65	12.00	0.52	4.10
0.06	0.66	14.25	0.47	4.45
0.07	0.66	13.54	0.44	3.93
0.08	0.66	12.66	0.45	3.76
0.09	0.64	11.37	0.36	2.62
0.10	0.64	11.82	0.28	2.11

Table 4

Photovoltaic parameters of DSCs with ARHC CEs prepared using different spray temperatures on FTO glass substrate by keeping the optimized PVP amount (0.06 g).

Spray temperature of FTO substrate/°C	V_{OC}/V	$J_{SC}/\text{mA cm}^{-2}$	FF	$\eta/\%$
50	0.64	11.17	0.40	2.88
75	0.65	13.39	0.58	5.27
100	0.65	13.89	0.62	6.06
150	0.68	13.10	0.55	4.89
200	0.68	12.12	0.53	4.37
250	0.68	13.00	0.47	4.15

3.6.3. DSC performance with different counter electrodes

Fig. 8 presents the photocurrent density – voltage (J - V) curves of the DSCs with ARHC, and Pt CEs, measured under irradiation of 100 mW/cm², and corresponding photovoltaic parameters of DSCs are summarized in Table 5.

As summarized parameters, the DSC with ARHC-CE shows the least conversion efficiency of 6.06 %. On the other hand, the cell with Pt CE shows a much higher efficiency of 8.21 % than ARHC CE. It can be seen that lower FF and J_{SC} in ARHC CE-based DSC compared with Pt-based cells are responsible for poor efficiency. On the other hand, a previous report by Kumarasinghe et al. showed that activated coconut shell charcoal-based counter electrodes developed using different method of activation had a conversion efficiency of 7.85% [23]. Moreover, Shun-jian Xu et al. have investigated twenty renewable bio-wastes derived carbon as green counter electrodes for DSCs. They noticed that the efficiency of DSCs developed using bio-waste-derived carbon materials from woods and leaves ranged from 1.23% to 1.91% and 1.07%–1.85%, respectively [24]. Nevertheless, those counter electrodes have shown

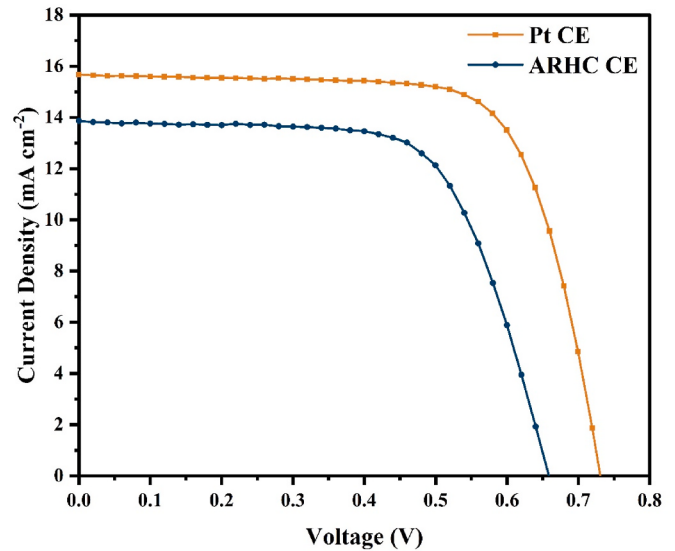


Fig. 8. J - V characteristics curves of DSCs with ARHC, and Pt CEs, measured under an illumination of 100 mW/cm².

Table 5

Photovoltaic parameters of DSCs with different counter electrodes.

Counter Electrode	V_{OC}/V	$J_{SC}/\text{mA cm}^{-2}$	FF	$\eta/\%$
Pt	0.73	15.67	0.72	8.21
ARHC	0.65	13.86	0.66	6.06

lower conversion efficiencies, when compared to those of the present study.

The defect sites in carbon materials serve as electro-catalytic sites [7]. In other words, if the degree of defects (I_D/I_G) is higher, the cell's electrocatalytic ability and associated J_{SC} would be both higher [25–27]. Therefore, the DSC with ARHC CEs, larger J_{SC} of the cell with ARHC film (13.86 mA cm^{−2}), may be due to a higher degree of defects in the former (I_D/I_G of the ARHC is 0.92). Nevertheless, when comparing the overall performance of ARHC-CE-based DSCs with reference Pt CE-based DSCs, cells prepared with ARHC-CE show low conversion efficiency. However, the findings of the current study reveal new possibilities to replace expensive Pt CE with low-cost ARHC-CE.

3.7. IPCE measurements of DSCs

Fig. 9 demonstrates the IPCE curves of DSCs with Pt and ARHC CEs. The broad curves cover almost the entire visible spectra from 300 nm to 800 nm wavelength range and exhibit IPCE peak values of 61%, and 56% at 500 nm–550 nm for DSCs with Pt, and ARHC CEs respectively. As can be seen from the IPCE values, a larger IPCE value is obtained for the cell with Pt CE than that of ARHC-CE. Because Pt CEs have a very low potential for the triiodide reduction reaction.

3.8. Electrochemical impedance spectroscopy (EIS) analysis of DSCs

To understand the electrocatalytic activities of the prepared CEs their EIS measurements were studied. The assembled DSCs were used to take EIS spectra. Fig. 10 shows the Nyquist plots of DSCs with Pt, and ARHC CEs, measured between frequencies of 10^{−2} – 10⁶ Hz. The inset within the figure displays the equivalent circuit diagram, which has been adjusted using NOVA software. Throughout this study, the photoanode parts of the cells were identical, the summarized data in Table 6 allows a deep insight into investigating the catalytic property of the CEs. The total ohmic resistance (R_s) corresponds to series resistance which represents the high frequency intercept on the real impedance axis in the

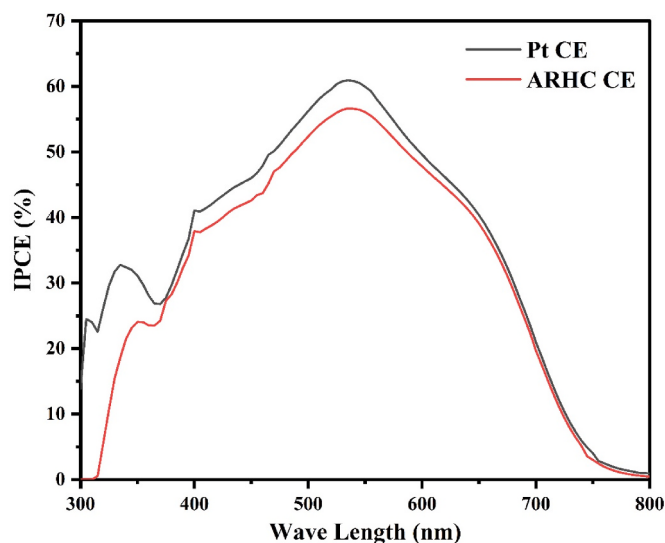


Fig. 9. IPCE spectra of DSC with Counter electrodes, consisting of Pt, and ARHC.

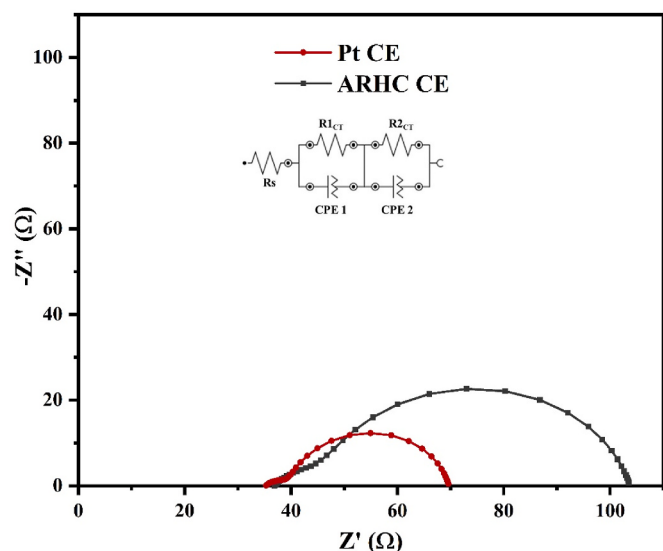


Fig. 10. Nyquist plots of counter electrodes based on Pt, and ARHC.

Table 6

Electron transport properties of their counter electrodes were determined by the EIS analysis.

CE	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	f_{max} (Hz)	τ_e (ms)
Pt	35.3	5.9	32.1	1.93	83.4
ARHC	36.9	13.1	61.2	2.81	56.6

Nyquist plot. R_{1CT} represents the charge transfer resistance at the CE/electrolyte interface. As shown in the Nyquist plot, the semicircle in the high-frequency region displays the R_{1CT} .

Notably, the R_{1CT} has a negative impact on the DSC performances in terms of FF and overall power conversion efficiency [28,29]. That means the greater R_{1CT} is responsible for a lower electron transfer rate between CE and electrolyte, resulting in poor performance of the cell [30–33]. It can be noticed that the R_s values of each CE are nearly similar. The R_{1CT} value for DSCs with Pt, and ARHC was found as 5.9, and 13.1 Ω respectively. As the comparison between ARHC and Pt CEs, the lower

R_{1CT} of the DSC with Pt CE shows higher efficiency and the most effectiveness for tri-iodide reduction than DSC based on ARHC-CE. Additionally, while Pt CEs, the standard choice for DSCs, exhibit superior effectiveness in tri-iodide reduction, ARHC CEs offer a cost-effective alternative to replace the expensive Pt counter electrode.

The electron lifetime (τ_e) was calculated from the Bode phase plots (Fig. 11) using the following equation.

$$\tau_e = 1/2\pi f_{max} \quad \text{Equation 2}$$

If a Bode phase plot shows that the peak characteristic has shifted from a higher frequency to a lower frequency, it indicates a faster transport process [34,35]. Table 6 depicts the extracted data from the Bode plots.

Lower resistance at CE/electrolyte (R_{1CT}) for the electron transport and longer τ_e leads to a higher charge collection rate of the photo-generated electrons, which improves the overall performances of DSCs [36–41]. The calculated τ_e of DSCs fabricated using Pt-based, and ARHC-based CEs are 83.4, and 56.6 ms respectively. It means that Pt-based CE has longer τ_e for the recombination process than ARHC CEs. This may have happened due to the high corrosive ability of iodide/triiodide redox electrolytes and attacks activated RH CEs. These factors may affect the slightly lower performance of DSC-based ARHC-CE compared to the DSC with Pt CE.

3.9. Cyclic voltammetric studies

To further study the electrochemical behavior of Pt and best-performance ARHC CEs, cyclic voltammetry (CV) measurements were taken. The cyclic voltammograms obtained for redox reaction I^-/I_3^- of both CEs were recorded using diluted iodide-based liquid electrolyte with the scan rate 30 mV s⁻¹ as shown in Fig. 12. Ag/AgCl and Pt rod were used as reference electrodes and counter electrodes respectively, in the CV setup. Also, Pt CE and prepared ARHC-CE were used as a working electrode at a time with an effective surface area of 1.0 cm².

In CVs of Pt CE, two distinctive sets of peaks assigned to the oxidation of I^- and reduction of I_3^- can be observed, respectively [42,43]. The relative oxidation peaks are assigned to redox reaction 1 and the reduction peaks are associated with redox reaction 2.

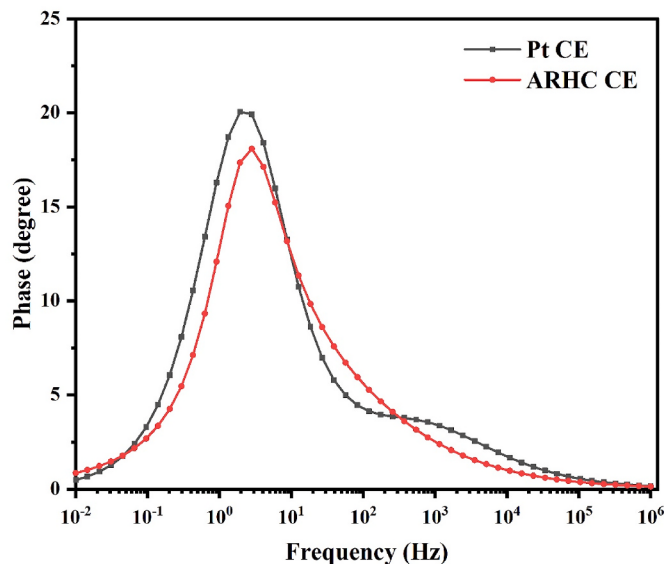


Fig. 11. Bode phase plots of DSCs constructed using Pt-based, and ARHC-based CEs.

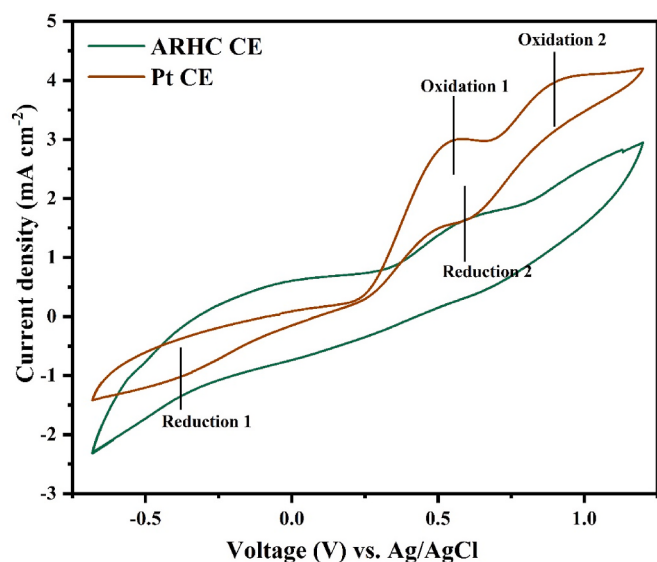
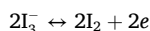


Fig. 12. Cyclic voltammograms taken with Pt and ARHC CEs using the three-electrode system with a 30 mV s⁻¹ in acetonitrile solution containing 10 mM LiI, 1 mM I₂, and 0.1 M LiClO₄.



Redox reaction 2

However, one set of oxidation and reduction peaks can be shown in ARHC-CE cyclic voltammograms. Due to Fig. 12, the current densities corresponding to the triiodide reduction peaks differ from Pt > ARHC. Theoretically, high current densities of the cathodic or reduction peak reason for the high catalytic activity of triiodide reduction [6,10]. Among most of the counter-electrode materials used for DSCs, Pt is the best catalytic counter-electrode material for the above reduction reaction. Also, ARHC consists of some impurities as indicated in the EDX spectrum (Fig. 6). Furthermore, the Broadening of the CVs and the peak shift of reactions are responsible for double-layer capacitance. The building up of double-layer capacitance is a disadvantage for DSCs. However, due to the porous nature of defects and impurities of ARHC, the double-layer capacitance of the ARHC-CE is larger than the Pt CE. Thus, it can be concluded further purification of ARHC is more important in enhancing the performance of ARHC-based DSCs.

4. Conclusion

The use of platinum electrodes as the CE in DSCs presents significant economic and environmental challenges. To address this issue, active carbon suitable to prepare CEs for DSCs was synthesized using the agricultural waste rice husk. In this study, we employed a simple spray pyrolysis method to prepare rice husk-activated carbon CEs. The DSC utilizing this activated rice husk carbon CE achieved a conversion efficiency of 6.06%, which is comparable to the 8.21% efficiency observed with a platinum electrode-based cell. Although the performance of the DSC based on activated carbon of rice husk CE is lower than that of the platinum-based, our findings open up new possibilities for exploring the use of acceptable agricultural biomass waste-derived carbons as viable and cost-effective alternatives to platinum CEs in DSCs.

CRediT authorship contribution statement

M.I.U. Weerasinghe: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **P.M.L. Kumarage:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **I.G.K.D. Amarathunga:** Methodology, Formal analysis. **T.M.W.J. Bandara:** Writing – review & editing, Validation, Supervision. **D. Velauthapillai:**

Writing – review & editing, Visualization, Validation, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **B.C. Karunarathne:** Software, Methodology, Data curation. **R. Punniamoorthy:** Writing – review & editing, Visualization, Validation. **R.M.G. Rajapakse:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **G.R.A. Kumara:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] S. He, L. Shang, Y. Gao, Y. Shi, F. Tan, X. Chen, G. Yue, Holistically modulating charge recombination via trisiloxane surface treatment for efficient dye-sensitized solar cells, *J. Alloys Compd.* 896 (2022) 162864, <https://doi.org/10.1016/j.jallcom.2021.162864>.
- [2] H.D.S. Cells, Holistically Optimizing Charge Carrier Dynamics Enables High-Performance Dye-Sensitized Solar Cells and Photodetectors, vol. 14, 2022, pp. 1–15, pubs.acs.org/doi/10.1021/acsami.2c13009?goto=supporting-info.
- [3] R. Madhu, V. Veeramani, S.M. Chen, J. Palanisamy, A.T. Ezhil Vilian, Pumpkin stem-derived activated carbons as counter electrodes for dye-sensitized solar cells, *RSC Adv.* 4 (2014) 63917–63921, <https://doi.org/10.1039/c4ra12585a>.
- [4] A.A. B. Madushani, P. Kumarasinghe, G. Kumara, L. Bandara, S. Lanka, Fabrication of floated graphite/graphene-based composite counter electrode for dye-sensitized solar cell, *Int. Res. J. Eng. Technol.* (2020) 2824–2829. www.irjet.net.
- [5] H. Wang, Y.H. Hu, Graphene as a counter electrode material for dye-sensitized solar cells, *Energy Environ. Sci.* 5 (2012) 8182–8188, <https://doi.org/10.1039/C2EE21905K>.
- [6] E.N. Jayaweera, G.R.A. Kumara, H.M.G.T.A. Pitawala, R.M.G. Rajapakse, N. Gunawardhana, H.M.N. Bandara, A. Senarathne, C.S.K. Ranasinghe, H. Huang, M. Yoshimura, Vein graphite-based counter electrodes for dye-sensitized solar cells, *J. Photochem. Photobiol. Chem.* 344 (2017) 78–83, <https://doi.org/10.1016/j.jphotochem.2017.05.009>.
- [7] Y.Y. Li, C.T. Li, M.H. Yeh, K.C. Huang, P.W. Chen, R. Vittal, K.C. Ho, Graphite with different structures as catalysts for counter electrodes in dye-sensitized solar cells, *Electrochim. Acta* 179 (2015) 211–219, <https://doi.org/10.1016/j.electacta.2015.06.007>.
- [8] T.N. Murakami, S. Ito, Q. Wang, M.K. Nazeeruddin, T. Bessho, I. Cesar, P. Liska, R. Humphry-Baker, P. Comte, P. Péchy, M. Grätzel, Highly efficient dye-sensitized solar cells based on carbon black counter electrodes, *J. Electrochem. Soc.* 153 (2006) A2255, <https://doi.org/10.1149/1.2358087>.
- [9] R. Kumar, P. Bhargava, Synthesis and characterization of carbon based counter electrode for dye sensitized solar cells (DSSCs) using organic precursor 2-2'Bipyridine (Bpy) as a carbon material, *J. Alloys Compd.* 748 (2018) 905–910, <https://doi.org/10.1016/j.jallcom.2018.03.181>.
- [10] G. Wang, D. Wang, S. Kuang, W. Xing, S. Zhuo, Hierarchical porous carbon derived from rice husk as a low-cost counter electrode of dye-sensitized solar cells, *Renew. Energy* 63 (2014) 1–7, <https://doi.org/10.1016/j.renene.2013.10.033>.
- [11] K. Divakara, M. Sakunthala, P.K. Kumarasinghe, B.C. Karunarathne, S. P. Dunuweera, R. Mudiyanse, G. Rajapakse, K. Tennakone, G. Rajanya, A. Kumara, Impact of 4-tertiary-butylpyridine in imidazolium iodide/triiodide redox couple-based dye-sensitized solar cells, *ACS Publ* 4 (2021) 9393–9401, <https://doi.org/10.1021/acsam.1c01587>.
- [12] M. Li, S. Ma, X. Zhu, Preparation of activated carbon from pyrolyzed rice husk by leaching out ash content after CO₂ activation, *Bioresources* 11 (2016) 3384–3396, <https://doi.org/10.15376/biores.11.2.3384-3396>.
- [13] A.H. Wazir, I.U. Wazir, A.M. Wazir, Preparation and characterization of rice husk based physical activated carbon, *Energy Sources, Part A Recover. Util. Environ. Eff.* (2020) 1–11, <https://doi.org/10.1080/15567036.2020.1715512>, 00.
- [14] Y. Shen, M. Ding, X. Ge, M. Chen, Catalytic CO₂ gasification of rice husk char for syngas and silica-based nickel nanoparticles production, *Ind. Eng. Chem. Res.* 54 (2015) 8919–8928, <https://doi.org/10.1021/acs.iecr.5b02677>.
- [15] Y. Liu, Y. Guo, W. Gao, Z. Wang, Y. Ma, Z. Wang, Simultaneous preparation of silica and activated carbon from rice husk ash, *J. Clean. Prod.* 32 (2012) 204–209, <https://doi.org/10.1016/j.jclepro.2012.03.021>.

- [16] C. Rong, S. Chen, J. Han, K. Zhang, D. Wang, X. Mi, X. Wei, Hybrid supercapacitors integrated rice husk based activated carbon with LiMn_2O_4 , *J. Renew. Sustain. Energy* 7 (2015), <https://doi.org/10.1063/1.4913965>.
- [17] T.X. Shang, R.Q. Ren, Y.M. Zhu, X.J. Jin, Oxygen- and nitrogen-co-doped activated carbon from waste particleboard for potential application in high-performance capacitance, *Electrochim. Acta* 163 (2015) 32–40, <https://doi.org/10.1016/j.electacta.2015.02.147>.
- [18] E.Y.L. Teo, L. Muniandy, E.P. Ng, F. Adam, A.R. Mohamed, R. Jose, K.F. Chong, High surface area activated carbon from rice husk as a high performance supercapacitor electrode, *Electrochim. Acta* 192 (2016) 110–119, <https://doi.org/10.1016/j.electacta.2016.01.140>.
- [19] X.F. Guo, G.J. Kim, Ultrafine carbon black produced by pyrolysis of polyethylene using a novel DC-thermal plasma process, *J. Phys. Chem. Solid* 69 (2008) 1224–1227, <https://doi.org/10.1016/j.jpcs.2007.10.139>.
- [20] Y. Chen, Y. Zhu, Z. Wang, Y. Li, L. Wang, L. Ding, X. Gao, Y. Ma, Y. Guo, Application studies of activated carbon derived from rice husks produced by chemical-thermal process - a review, *Adv. Colloid Interface Sci.* 163 (2011) 39–52, <https://doi.org/10.1016/j.cis.2011.01.006>.
- [21] Y. Guo, D.A. Rockstraw, Activated carbons prepared from rice hull by one-step phosphoric acid activation, *Microporous Mesoporous Mater.* 100 (2007) 12–19, <https://doi.org/10.1016/j.micromeso.2006.10.006>.
- [22] L.K. Lazzari, M.V.G. Zimmermann, D. Perondi, V.B. Zampieri, A.J. Zattera, R.M. C. Santana, Production of carbon foams from rice husk, *Mater. Res.* 22 (2019) 1–8, <https://doi.org/10.1590/1590-5373-MR-2019-0427>.
- [23] K.D.M. Kumarasinghe, G.R.A. Kumara, R.M.G. Rajapakse, D.N. Liyanage, K. Tennakone, Activated coconut shell charcoal based counter electrode for dye-sensitized solar cells, *Org. Electron.* 71 (2019) 93–97, <https://doi.org/10.1016/j.orgel.2019.05.009>.
- [24] S. Xu, C. Liu, J. Wieczorek, 20 renewable biowastes derived carbon materials as green counter electrodes for dye-sensitized solar cells, *Mater. Chem. Phys.* 204 (2018) 294–304, <https://doi.org/10.1016/j.matchemphys.2017.10.056>.
- [25] C.K. Hsieh, M.C. Tsai, C.Y. Su, S.Y. Wei, M.Y. Yen, C.C.M. Ma, F.R. Chen, C.H. Tsai, A hybrid nanostructure of platinum-nanoparticles/graphitic-nanofibers as a three-dimensional counter electrode in dye-sensitized solar cells, *Chem. Commun.* 47 (2011) 11528–11530, <https://doi.org/10.1039/c1cc15049a>.
- [26] J. Xia, L. Chen, S. Yanagida, Application of polypyrrole as a counter electrode for a dye-sensitized solar cell, *J. Mater. Chem.* 21 (2011) 4644–4649, <https://doi.org/10.1039/c0jm04116e>.
- [27] K.C. Huang, J.H. Huang, C.H. Wu, C.Y. Liu, H.W. Chen, C.W. Chu, J.T.S. Lin, C. L. Lin, K.C. Ho, Nanographite/polyaniline composite films as the counter electrodes for dye-sensitized solar cells, *J. Mater. Chem.* 21 (2011) 10384–10389, <https://doi.org/10.1039/c1jm10576k>.
- [28] A. Atli, A. Atilgan, C. Altinkaya, K. Ozel, A. Yildiz, St. Lucie cherry, yellow jasmine, and madder berries as novel natural sensitizers for dye-sensitized solar cells, *Int. J. Energy Res.* 43 (2019) 3914–3922, <https://doi.org/10.1002/er.4538>.
- [29] Y. Gao, M. Cui, S. Qu, H. Zhao, Z. Shen, F. Tan, Y. Dong, C. Qin, Z. Wang, W. Zhang, Z. Wang, Y. Lei, Efficient organic solar cells enabled by simple non-fused electron donors with low synthetic complexity, *Small* 18 (3) (2022) 18, <https://doi.org/10.1002/smll.202104623>.
- [30] C. Altinkaya, A. Atli, A. Atilgan, K. Salimi, A. Yildiz, Facile fabrication of low-cost low-temperature carbon-based counter electrode with an outstanding fill factor of 73% for dye-sensitized solar cells, *Int. J. Energy Res.* 44 (2020) 3160–3170, <https://doi.org/10.1002/er.5174>.
- [31] X. Meng, C. Yu, X. Zhang, L. Huang, M. Rager, J. Hong, J. Qiu, Z. Lin, Active sites-enriched carbon matrix enables efficient triiodide reduction in dye-sensitized solar cells: an understanding of the active centers, *Nano Energy* 54 (2018) 138–147, <https://doi.org/10.1016/j.nanoen.2018.09.070>.
- [32] G.R. Li, X.P. Gao, Low-cost counter-electrode materials for dye-sensitized and perovskite solar cells, *Adv. Mater.* 32 (2020), <https://doi.org/10.1002/adma.201806478>.
- [33] C.S. Wu, T.W. Chang, H. Teng, Y.L. Lee, High performance carbon black counter electrodes for dye-sensitized solar cells, *Energy* 115 (2016) 513–518, <https://doi.org/10.1016/j.energy.2016.09.052>.
- [34] H.H. Thi Vu, T.S. Atabaev, J.Y. Ahn, N.N. Dinh, H.K. Kim, Y.H. Hwang, Dye-sensitized solar cells composed of photoactive composite photoelectrodes with enhanced solar energy conversion efficiency, *J. Mater. Chem. A* 3 (2015) 11130–11136, <https://doi.org/10.1039/c5ta02363g>.
- [35] Y. Gao, Z. Xiao, M. Cui, M.I. Saidaminov, F. Tan, L. Shang, W. Li, C. Qin, L. Ding, Asymmetric Π -bridge engineering enables high-permittivity benzo[1,2-B:4,5-b']difuran-Conjugated polymer for efficient organic solar cells, *Adv. Mater.* 36 (36) (2024) 2306373, <https://doi.org/10.1002/adma.202306373>, 9.
- [36] X. Pan, C. Chen, K. Zhu, Z. Fan, TiO_2 nanotubes infiltrated with nanoparticles for dye sensitized solar cells, *Nanotechnology* 22 (2011), <https://doi.org/10.1088/0957-4484/22/23/235402>.
- [37] D. Zhang, X. Li, S. Chen, Z. Sun, X.J. Yin, S. Huang, Performance of dye-sensitized solar cells with various carbon nanotube counter electrodes, *Microchim. Acta* 174 (2011) 73–79, <https://doi.org/10.1007/s00604-011-0597-0>.
- [38] D.W. Zhang, X.D. Li, S. Chen, F. Tao, Z. Sun, X.J. Yin, S.M. Huang, Fabrication of double-walled carbon nanotube counter electrodes for dye-sensitized solar cells, *J. Solid State Electrochem.* 14 (2010) 1541–1546, <https://doi.org/10.1007/s10008-009-0982-3>.
- [39] X. Qi, C. Song, W. Zhang, Y. Shi, Y. Gao, H. Liu, R. Chen, L. Shang, H. Tan, F. Tan, H.L. Wang, Bidirectional targeted therapy enables efficient, stable, and eco-friendly perovskite solar cells, *Adv. Funct. Mater.* 33 (2023) 1–9, <https://doi.org/10.1002/adfm.202214714>.
- [40] Y. Gao, Z. Shen, F. Tan, G. Yue, R. Liu, Z. Wang, S. Qu, Z. Wang, W. Zhang, Novel benzo[1,2-b:4,5-b']difuran-based copolymer enables efficient polymer solar cells with small energy loss and high V_{OC} , *Nano Energy* 76 (2020), <https://doi.org/10.1016/j.nanoen.2020.104964>.
- [41] J. Huang, S. He, W. Zhang, A. Saparbaev, Y. Wang, Y. Gao, L. Shang, G. Dong, L. Nurumbetova, G. Yue, Y. Tu, Efficient and stable all-inorganic $\text{CsPbI}_2\text{Br}_2$ perovskite solar cells enabled by dynamic vacuum-assisted low-temperature engineering, *Sol. RRL* 6 (2022), <https://doi.org/10.1002/solr.202100839>.
- [42] M.A.K.L. Dissanayake, J.M.K.W. Kumari, G.K.R. Senadeera, T. Jaseetharan, J. Weerasinghe, H. Anwar, A low-cost, vein graphite/tin oxide nanoparticles based composite counter electrode for efficient dye-sensitized solar cells, *Mater. Sci. Eng. B* 273 (2021) 115440, <https://doi.org/10.1016/j.mseb.2021.115440>.
- [43] M.A.K.L. Dissanayake, J.M.K.W. Kumari, G.K.R. Senadeera, H. Anwar, Low cost, platinum free counter electrode with reduced graphene oxide and polyaniline embedded SnO_2 for efficient dye sensitized solar cells, *Sol. Energy* 230 (2021) 151–165, <https://doi.org/10.1016/j.solener.2021.10.022>.