Integration of 3D interconnected sodium hydroxide modified biochar with the tile-like architecture of cobalt oxides for asymmetric supercapacitors

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Abstract

Two state-of-the-art electrodes were successfully synthesized and used to assemble both symmetric and asymmetric type supercapacitors. 3DFAB was fabricated by direct pyrolysis of green macroalgae in the presence of NaOH. Possible mechanisms of NaOH activation is proposed, which explains the formation of oxygen functional groups through quick penetration of OH- and NaOH into the vacancies. To obtain CoTLM, the tile-like architecture of cobalt oxides was introduced to the 3D interconnected functional algal biochar (3DFAB) by a simple one-pot hydrothermal method under mild conditions. For the symmetric supercapacitors, the maximum specific capacitance of RAB, 3DFAB, and CoTLM were 177 F g⁻¹, 322 F g⁻¹, and 529 F g⁻¹ at a scan rate of 5mVs⁻¹. Regarding cobalt-based asymmetric systems, the maximum capacitance for the RAB//CoTLM and 3DFAB//CoTLM were ∼300 F g⁻¹ and 400 F g⁻¹, respectively. The 3DFAB//CoTLM showed a higher energy density compared with RAB//CoTLM, while the RAB//CoTLM exhibited better cycling performance (99.1% of its initial capacitance after 4k cycles at the current density of 4 A g⁻¹).

Keywords: Asymmetric supercapacitor; 3D interconnected; cobalt; Macroalgae; Sodium hydroxide
Nomenclature

| Term                                                                 | Symbol | Method                                                                 |
|----------------------------------------------------------------------|--------|------------------------------------------------------------------------|
| Electrical Double-Layer Capacitance                                  | EDLC   | Continuous Cyclic Voltammetry                                          |
| Continuous Cyclic Voltammetry                                         | CCV    |                                                                        |
| Asymmetric Supercapacitor Cell                                        | ASC    | Asymmetric Supercapacitor Cell                                          |
| Fourier Transform Infrared                                            | FTIR   |                                                                        |
| Tile-like Microstructure containing Cobalt oxides                     | CoTLM  | X-ray Photoelectron Spectroscopy                                        |
| X-ray Photoelectron Spectroscopy                                      | XPS    |                                                                        |
| 3D interconnected mesopores network                                  | 3DFAB  | Field Emission Scanning Electron Microscopy                             |
| Field Emission Scanning Electron Microscopy                           | FESEM  |                                                                        |
| Specific Capacitances                                                | SC     | Brunauer-Emmette-Teller                                                |
| Brunauer-Emmette-Teller                                              | BET    |                                                                        |
| Alkali and Alkaline Earth Metals                                     | AAEM   | X-ray Diffraction                                                      |
| X-ray Diffraction                                                     | XRD    |                                                                        |
| Electrochemical Impedance Spectroscopy                               | EIS    | Cyclic Voltammetry                                                     |
| Cyclic Voltammetry                                                    | CV     |                                                                        |
| Polytetrafluoroethylene                                               | PTFE   | Galvanostatic Charge/Discharge                                          |
| Galvanostatic Charge/Discharge                                        | GCD    |                                                                        |

Introduction

Industrial and agricultural pollutants have significantly changed the level of nutrients, primarily nitrogen and phosphorus, in oceans, seas, and rivers\(^1\). These changes, directly or indirectly, cause damage to the environment on a global scale. The eutrophication, the excessive blooming of macroalgae, is a visible, alarming, and devastating phenomenon occurring as a result of such human activities. To mitigate the issue of eutrophication, many researches have been conducted to evaluate the viability of using these harmful microalgae as a source of biofuel \(^3,4\). However, macroalgae biofuel production has not been fully commercialized, due to the major economic and technical challenges. To minimize waste and improve the efficiency of the circular economy, biochar obtained as a byproduct of the thermochemical conversion of macroalgae could be further processed for versatile applications in energy conversion and storage sectors\(^5-9\). The best-known example is the application of biochar as a promising alternative to its commercial competitors in supercapacitors due to their obvious advantages such as low cost, accessibility, reduced environmental impact, and good stability\(^10,11\).
Algal biochar has a unique advantage over agricultural wastes in the way that macroalgae undergoes self-activation and nitrogen self-doping during the thermal process due to the abundance of potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), and nitrogen (N) that exist in the algae structure. However, there is still much work to be done in reaching the desired electrochemical properties in supercapacitors by rationally integrating the physical and chemical modification methods. Algal biochar needs to be further processed to achieve a highly improved EDLC and pseudocapacitance performance. Most state-of-the-art modified biochar composites with excellent capacitive performance have been reviewed comprehensively by Norouzi et al. The simplest and most popular chemical surface modification is the use of NaOH or/and KOH activators before or after the thermal process. For example, Hu et al. successfully synthesized porous particulate activated carbons from low sulfonate content alkaline lignin by hydrothermal carbonization in the presence of NaOH and NaOH modifiers. The synthesized material showed a hierarchical structure with improved $S_{\text{BET}}$, functional groups, and EDLC performance. In addition to chemical modification, it is beneficial to simultaneously enhance the pseudocapacitance of the sample by introducing pseudocapacitive materials into the biochar structure. To this end, transition metal oxides or hydroxides are usually embedded in the porous structure of the surface-modified biochar. Among the available pseudocapacitive materials, cobalt hydroxides or oxides are favorable candidates for application in electrochemical capacitors due to their low cost, great reversibility, high conductivity, multiple oxidation states, and high specific capacitance. Cobalt oxide ($\text{Co}_3\text{O}_4$) has an extremely high theoretical specific capacitance of up 3560 F g$^{-1}$, which has been recently receiving more attention within the electrochemistry research groups.

Apart from designing a hybrid biochar electrode, selecting two dissimilar electrode materials with well-separated potential windows, called Asymmetric supercapacitors (ASCs), plays a vital role in reaching higher energy density, power density, and cycle life. In this study, a cost-effective ACSs was fabricated using a new interconnected tile-like microstructure containing cobalt oxide particles, referred to as CoTLM, and functional algal biochar composed of a 3D interconnected mesopores network (3DFAB). The CoTLM composites were synthesized by impregnation of $\text{Co(NO}_3\text{)}_6\cdot\text{H}_2\text{O}$ on the surface of algal biochar under hydrothermal carbonization. FAB was prepared by direct pyrolysis using green macroalgae as the carbon precursor and NaOH as the activator.
Results and dissuasions

FTIR analysis was carried out to indicate the rate and degree of decomposition during the synthesis based on functional groups. All three samples have similar FTIR spectra, but at different intensities (Fig. 2a). The spectra of glycosyl-units of cellulose are detected in the range of 1150-1070 cm$^{-1}$ due to the stretching vibrations of CH-, OH-, and CH$_2$- groups$^{23}$. The strongest peaks at these ranges are observed in the CoTLM spectrum, showing the more intense glycosidic bond-breaking reactions. The FT-IR spectrum of CoTLM exhibits a broader peak at 2000-3400 cm$^{-1}$ which can be attributed to its higher hydrophilic and conductive nature. Peaks at 1457, 1592, and 1710 cm$^{-1}$ are assigned to the ester and carboxylic acid functional groups in cellulose-based polysaccharides$^{24,25}$. These peaks have been pronounced in 3DFAB, as compared to the RAB, as the result of a series of reactions which have been shown in Eq 1-6 and Fig. 1. During the pyrolysis process, NaOH vigorously reacts with carbonyl, hydroxyl, carboxyl, ether, and ester functional groups to produce free radicals as well as a number of vacancies. At the same time, many vacancies are created due to the NaOH reaction with the C–C and C–H groups. Then, many oxygen functional groups are formed by quick penetration of OH- and NaOH into the vacancies. Finally, NaOH reacts with oxygen functional groups over in carbon fragments at 400-700 °C, which can produce K$_2$CO$_3$ (Eq 1-6).

According to the literature, most of the acidic functional groups attached to the surface of 3DFAB should react with cobalt ions (CO$^{2+}$ and CO$^{3+}$) during HTC to produce water and cobalt nanoparticles (eq 7 and 8). Thus, a lower intensity of -O containing groups was excepted, but was not found. This could be due to the improved hydrolysis reactions in HTC by which polysaccharides as macro-intermediates are produced from the unreacted cellulose remaining after the pyrolysis.

$$6\text{NaOH} + 2\text{C} \rightarrow 2\text{K}_2\text{CO}_3 + 2\text{Na} + 3\text{H}_2$$  \hspace{1cm} (1)
$$\text{NaOH} + (\text{-COOH})/(\text{- O - C = O}) \rightarrow \text{Na}_2\text{CO}_3 + \text{Na} + \text{H}_2 + \text{CO}_2$$  \hspace{1cm} (2)
$$\text{NaOH} + (\text{- C = O})/(\text{C - O - C}) \rightarrow \text{Na}_2\text{CO}_3 + \text{Na} + \text{H}_2 + \text{CO}$$  \hspace{1cm} (3)
$$\text{NaOH} + (\text{- O - CH}_3) \rightarrow \text{Na}_2\text{CO}_3 + \text{Na} + \text{H}_2 + \text{CH}_4$$  \hspace{1cm} (4)
$$\text{NaOH} + (\text{C - OH}) \rightarrow \text{Na}_2\text{CO}_3 + \text{Na} + \text{H}_2\text{O} + \text{H}_2$$  \hspace{1cm} (5)
$$\text{NaOH} + (\text{C - H}) \rightarrow \text{Na}_2\text{CO}_3 + \text{Na} + \text{H}_2$$  \hspace{1cm} (6)
\[ \text{Co}^{2+} - e \rightarrow \text{Co}^{3+} \]  
(7)

\[ 2\text{Co}^{3+} + \text{Co}^{2+} + 8\text{OH}^{+} + 3\text{DFAB} \rightarrow \text{CoTLM} + 4\text{H}_2\text{O} \]  
(8)

Figure 1. Possible mechanism of NaOH activation for the synthesis of 3FAB.

Fig. 2b shows XRD patterns of RAB, 3DFAB, and CoTLM. The crystalline region of cellulose found at 2θ about 22.45° and 34.25°. For modified samples, since the experiments were performed in a harsher synthetic condition, strong peaks assigned to cellulose lost their intensity. In other words, for 3DFAB, and CoTLM, an amorphous structure and disordered graphitic (002) plane found at Bragg’s angle between 20° and 30° due to the crystalline-to-amorphous transformation of cellulose under intensive thermal conditions. Other sharp peaks at 2θ = 30.34°, 32.4°, 36.99°, 40.41°, 44.00°, 48.47°, 49.43°, 58.38°, and 61.64° are related to one of the calcium-based crystalline structures. Three identified phases are CCaO₃, Ca₆.₀₀C₃.₀₀O₁₈.₀₀, Ca₆.₀₀C₆.₀₀O₁₈.₀₀, and Ca₆.₀₀C₆.₀₀O₁₈.₀₀. In the case of CoTLM, peaks at 19.0°, 31.2°, 36.8°,
38.5°, 44.8°, 55.6°, 59.3°, 65.2°, and 77.3° confirm the crystalline structure of Co$_3$O$_4$, which is in accordance with the Joint Committee on Powder Diffraction Standard (JCPDS No. 00-042-1467)$^{27}$.

![Figure 2. FT-IR spectra (a) and XRD patterns (b) of RAB, 3DFAB, CoTLM](image)

Fig. 3a shows that the raw biochar derived from green macroalgae has an olive-shaped morphology with hollow macropores which are evenly spread with an average diameter of approximately 300 nm wide and 80 nm long. One interesting finding is that the olive-shaped morphology of RAB completely transformed into the circular-shaped structure in which pores are interconnected in the three-dimensional structure of 3DFAB (Fig. 3b). Fig. 1 and equations 1-6 explain the reason behind this morphology change through possible chemical reaction pathway of NaOH activation during biomass pyrolysis. These reactions resulted in an advanced morphology due to the release of large amounts of gaseous products. The 3D interconnected functionalized mesopores network can not only improve the accessible inner/outer surfaces but also facilitates the formation of Co$_3$O$_4$ via improved impregnation of cobalt salt solution using functional groups$^{12}$. The synthesized CoTLM possesses multilayered structures made from hierarchical nanosheets, which make it an advanced material with a tile-like microstructure (see Figure 3c). This architecture has already been observed by Shurui Liu et al$^{28}$. The unique hierarchical architecture of CoTLM provides a continuous pathway for electrons and shorten diffusion pathways for ions, thereby making it a great candidate for charge storage purposes.

Furthermore, after applying chemical and/or physical modifications on the green algae, surface elemental distribution in 3DFAB and CoTLM was changed significantly, which was verified by EDS analyses. The
quantitative results of the EDS are given in Table 1. Approximately 21% of the RAB’s surface is found to be covered by alkali and alkaline earth metals (AAEMs) such as sodium, potassium, calcium, and magnesium. These elements belong to the ash portion of the algae. The RAB contains 15% of sulfur and silica, which are considered essential micronutrients for the normal growth of algae\textsuperscript{29}. Oxygen content in 3DFAB has more than doubled due to the elimination of AAEMs by NaOH treatment and acid reflux. However, improved oxygen contents in CoTLM are mostly related to the attachment of oxygen functional groups produced under the hydrothermal treatment. Based on surface oxygen contents, we conclude that part of the CoTLM surface were developed by oxygen functional groups which make them more polar and hydrophilic than the original biochar derived from green algae. During the HTC in the presence of Co(NO\textsubscript{3})\textsubscript{6}H\textsubscript{2}O, cobalt particles were efficiently dispersed over the surface and caused improved oxidation-reduction reactions (pseudocapacitance) and higher electrical conductivity of the sample.

Table 1. EDS analyses of RAB, 3DFAB, and CoTLM prepared from green macroalgae.

| Element | C   | O   | N   | Na  | Mg  | Al  | Si  | S   | K   | Ca  | Fe  | Co  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| RAB     | 41.12 | 22.00 | -   | 1.21 | 1.24 | 0.75 | 2.32 | 13.0 | 2.92 | 15.3 | 0.15 | -   |
| 3DFAB   | 36.47 | 55.78 | 4.00 | -   | -   | -   | -   | 1.92 | 1.83 | -   | -   | -   |
| CoTLM   | 22.69 | 31.18 | -   | -   | -   | -   | -   | 1.54 | 2.52 | -   | -   | 2.23 | 39.84 |

Figure 3. FESEM images of the RAB (a), 3DFAB (b), and CoTLM (c)
Fig. 4 displays the N$_2$ adsorption-desorption isotherms, and BJH pore diameters of RAB, 3DFAB, CoTLM samples. All the N$_2$ adsorption-desorption isotherms exhibited the same kinetic of the reaction with a typical IV hysteresis loop at a relative pressure between 0.45 and 0.95 which confirms the hierarchical porous structure of samples$^{30-32}$. The majority of RAB pore volume is in the range of 0.10 cm$^2$ g$^{-1}$ nm$^{-1}$. However, the pore volume in 3DFAB and CoTLM samples fluctuates between 0.10 and 0.14 cm$^2$ g$^{-1}$ nm$^{-1}$, owing to the 3D architecture that occurred after the treatment. BET surface area of RAB, 3DFAB, and CoTLM were 243, 1020, and 605 m$^2$ g$^{-1}$, respectively. The characterization results reveal that both 3DFAB and CoTLM have a higher surface area, larger pore volume, and smaller pore diameter compared to the original biochar. The higher surface area and interconnected 3D pore network in the 3DFAB could be due to reaction 1 (Eq1) in which carbon reacts vigorously with sodium hydroxide to form Na$_2$O$_2$ along with hydrogen and carbon dioxide gas. Considering the superior textural properties of 3DFAB, it might be a highly promising start material for accommodating conductive materials in nanoscale. Herein, CoTLM was obtained through the dispersion of cobalt oxide particles within the interior of the interconnected 3D pore network of 3DFAB. CoTLM can not only facilitate charge transfer and ion diffusion but also take advantage of the pseudocapacitive nature of Co$_3$O$_4$ nanoparticles$^{33}$.

![Figure 4](image_url)

**Figure 4.** N$_2$ adsorption/desorption isotherm and pore size distributions (BJH) of the RAB, 3DFAB, CoTLM (a), Raman analyses (b)

Raman spectroscopy was performed to further analyze the carbon structure of RAB, 3DFAB, and CoTLM. According to the Raman spectra of samples (Fig. 4b), two main peaks were recorded at around 1345 cm$^{-1}$ (D band) and 1570 cm$^{-1}$ (G band) which are ascribed to the turbostratic and ideal graphitic carbon structure.
$I_D/I_G$ can reflect the disordered degree in the modified samples. The $I_D/I_G$ ratio for RAB, 3DFAB and CoTLM was 0.91, 1.05, and 1.65, respectively. Raman spectrum of CoTLM shows some characteristic peaks at 486, 529, 608, and 678 cm$^{-1}$, which are related to the vibrational modes of $E_g$, $F_{2g}$, $F_{2g}$, and $A_{1g}$, respectively.$^{34}$

**Electrochemical performance**

**CV measurements.** Fig. 5a gives typical cyclic voltammetry (CV) curves of the RAB, 3DFAB, and CoTLM at a scan rate of 50 mV s$^{-1}$. The CV of RAB, 3DFAB, CoTLM were in the range of -0.85-0.05 V, -0.9-0.1 V, and -0.1-0.9 V (vs. Ag/AgCl), respectively. The slight shift toward higher voltages in the redox potential of CoTLM, resulting from the unique 3D morphology and structure of the electrode material, shows the more polar nature of CoTLM.$^{28}$ Fig 5b-d shows typical CV curves of all three state of the art electrodes at various scan rates of 5 to 100 mV S$^{-1}$. They all have shown a quasi-rectangular shape even at the highest applied scan rate (100 mV S$^{-1}$), which is an indication of their excellent charge transfer capability.$^{21,35,36}$ The closest shape to an ideal rectangular can be found in 3DFAB (Fig. 5c), which might result from its ordered interconnected 3D pore network and superior surface area. The slower scan rate gives the electrolyte ions sufficient migration time to penetrate better within the interior of the porous carbons. At higher scan rates, electrolyte ions can only accumulate on the outer surface of samples.$^{22,37}$ The potential window of CoTLM is in the positive potential (vs. Ag/AgCl); while the potential window of 3DFAB is in the negative potential (vs. Ag/AgCl). The stable shape of CV in the high scan rate along with negative potential window make 3DFAB a good choice for negative electrodes. For the same reason above, CoTLM is suitable for positive electrodes in a full system. In the asymmetric system the positive electrodes is able to store energy with both faradic and non-faradic mechanism.
Figure 5. Electrochemical performance of the RAB, 3DFAB, and CoTLM electrodes. Cyclic voltammograms at 50 mV s⁻¹ (a); Cyclic voltammograms RAB, 3DFAB, and CoTLM at increasing rates from 5 to 100 mV s⁻¹(b,c,d);

CCV measurements. Fig. 6 shows the cyclic performance of the RAB, 3DFAB, CoTLM under 4000 cycles at the scan rate of 50 mV s⁻¹. For the CoTLM electrode, 5% of the capacitance is dropped due to the volume alternation in the electrode material caused by electrolyte intercalation and deintercalation reactions during long potential cycling. However, two other non-metal-modified electrodes, RAB and 3DFAB, exhibited superior cycling stability with 100.9% and 101.5% retention of their initial capacitance after 4000 cycles, respectively. This phenomenon has already been reported in the literature as the gradual activation of the surface with increasing the number of cycles. The results indicate that the electrochemical stability of the 3DFAB is higher than that of others, which makes it a suitable electrical double layer capacitor and a great candidate for accommodating pseudocapacitors.
Figure 6. 3D-CCV curves of the RAB, 3DFAB, and CoTLM electrodes measured at a scan rate of 50 mV s\(^{-1}\) (a, b, c), variation of the specific capacitance of the RAB, 3DFAB, and CoTLM electrodes with CCV method as a function of the number of cycles at 50 mV s\(^{-1}\) (d, e, f).

Galvanostatic charge-discharge (GCD) measurements. GCD curves of RAB, 3DFAB, and CoTLM are recorded and shown in Fig. 7a-c. The measurements were performed at current densities ranging from 1 to 16 A g\(^{-1}\). They all have symmetrical triangular shapes with any notable IR drop, suggesting their excellent charging-discharging behavior\(^{39,40}\). The triangular, linear, symmetric, and very sharp curved reflects their reversible behavior, high coulombic efficiency, and ideal capacitor performance.

Capacitance retention as a function of cycle number, at the current density of 1 A g\(^{-1}\), is plotted for RAB, 3DFAB, and CoTLM in Fig. 7d-f, respectively. As shown, three electrodes have a nearly identical capacitance drop after 4000 cycles. In all samples, the capacitance is promoted around 1%, indicating their
superior cyclic performance. This slight increase in capacitance after 4000 cycles is due to the improved access of electrolyte ions to the new activated sites at higher cycles\textsuperscript{12}.

![Graphs and images](image_url)

Figure 7. GCD of RAB, 3DFAB, and CoTLM at the current densities rates from 1 to 16 A g\(^{-1}\) (a, b, c); and cyclic performance of the RAB, 3DFAB, and CoTLM electrodes at the current density of 4 A g\(^{-1}\) (d, e, f)

EIS measurements. Charge transfer kinetics and ion diffusion rates were studied by EIS analysis. The Nyquist plots of RAB, 3DFAB, and CoTLM are shown in Fig. 8. EIS measurements were conducted at the frequency range from 0.01 to 100 kHz at a potential of about -0.45 V with alternate amplitude voltage of 5 mV. EIS data can be fitted by the equivalent circuit. Charge transfer resistance (R\(_{ct}\)) and ohmic resistance (R\(_s\)) were obtained through calculation of the semicircle diameter in the high-frequency regions and intercept of the real axis in the Nyquist diagrams, respectively. The CoTLM electrode shows a lower R\(_{ct}\) (2.6 \(\Omega\)) than that of RAB (5.1 \(\Omega\)) and 3DFAB (3.9 \(\Omega\)), confirming its remarkable electrical conductivity. Moreover, a higher slope is recorded for CoTLM electrode, revealing lower R\(_s\) (0.71 \(\Omega\)) in this electrode as
compared to RAB (0.84 Ω) and 3DFAB (81 Ω). The Warburg resistance, symbol $Z_w$, is the straight line at low-frequency regions. These lines show the variations in ion diffusion path lengths. As seen in Table 2, RAB, 3DFAB, and CoTLM have a $Z_w$ of 0.11, 0.13, 0.21 Ω, respectively. We can conclude that modification of RAB resulted in shorter ion diffusion paths and fewer barriers to ion movement\textsuperscript{41}.

![Nyquist plots of the RAB, 3DFAB, and CoTLM electrodes.](image)

Figure 8. Nyquist plots of the RAB, 3DFAB, and CoTLM electrodes.

Table 2. Calculated Values of $R_s$, CPE, $R_{ct}$, $Z_w$, and $C_f$ through CNLS Fitting of the Experimental Impedance Spectra Based upon the Proposed Equivalent Circuit

|       | RAB   | 3DFAB | CoTLM |
|-------|-------|-------|-------|
| $R_s$ (mOhm) | 0.84  | 0.78  | 0.71  |
| $C_{dl}$ (mF)  | 0.5   | 1.5   | 1.9   |
| $R_{ct}$ (Ohm) | 5.1   | 4.3   | 2.6   |
| $Z_w$ (MMho)   | 0.11  | 0.14  | 0.18  |
Electrochemical performances of the and 3DFAB//CoTLM ASC devices

For the ASC, 3DFAB has been considered as a positive faradic electrode due to its superior surface area and suitable potential window. On the other hand, CoTLM showed a stable and suitable potential window in the region of negative chosen electrodes. The working potential range of 3DFAB was -0.9–0 V, while that of CoTLM was -0.1–0.9 V. Thus, the cell voltage of this two-electrode combination has extended up to 1.7 V, which is significantly higher than that obtained in symmetric type supercapacitors. CV diagrams and charge/discharge curves of 3DFAB//CoTLM devices are shown in Fig. 9a and b. All the CV curves of the ASC devices remained unchanged, indicating that electrons and ions can easily move within the pore structure of the electrodes even at 100 mV s$^{-1}$. At the same time, charge-discharge curves have almost retained their symmetrical shape at different current densities, suggesting their high coulombic efficiency and good electrochemical reversibility of these two asymmetric systems.

![Figure 9. CV curves at different scan rates of 3DFAB//CoTLM (a), and charge/discharge curves under different current densities of 3DFAB//CoTLM (b)](image)
Fig. 10a shows 3D-CCV curves of 3DFAB//CoTLM electrode measured at a scan rate of 50 mV s\(^{-1}\) for 4000 cycles. As shown in Fig. 10b, the asymmetric systems showed superior cyclic stability and during the cycling, the additional peaks did not appear. Up to 98.5\% of the capacitance was retained for 3DFAB//CoTLM, The results were further processed into a Capacitance-Cycle number diagram to clarify the above statements.

![Fig. 10a: 3D-CCV curves of 3DFAB//CoTLM electrode.](image)

![Fig. 10b: Capacitance Retention (%) vs. Cycle Number.](image)

Figure 10. 3DFAB//CoTLM asymmetric systems measured at a scan rate of 50 mV s\(^{-1}\) (a), variation of the specific capacitance of the 3DFAB//CoTLM cell with CCV method as a function of the number of cycles at 50 mV s\(^{-1}\) (b)

To further support the above results, the cycle performance of 3DFAB//CoTLM electrode at the current density of 4 A g\(^{-1}\) is shown in Fig. 11a. Notably, 3DFAB//CoTLM electrode retained 99.1\% of its initial capacitance after 4000 cycles at the current density of 4 A g\(^{-1}\). Although the capacity decay after long-term cycling for asymmetric cobalt-based electrodes has been observed previously, the reasons have remained somewhat uncertain. There are three main hypotheses for such phenomenon: i) slight changes in ternary oxides and/or hydroxide are caused by intensive reaction with KCl, and ii) damage in the morphology of tile-like microstructure with a 3D architecture was due to the long-term cycling test.

Energy density and power density are two main factors that should be considered in scaling up the ACS devices. Fig. 11b shows the Ragone plots of the 3DFAB//CoTLM electrode. The energy density acquired from the 3DFAB//CoTLM ASC device is 54.44 Wh kg\(^{-1}\) with a power density of 800 W kg\(^{-1}\), which is significantly larger than those reported for cobalt and iron-based composite ASCs\(^{28}\).
Green macroalgae wastes (*Cladophora glomerata*) were collected by hand from different locations of the Speed River, Guelph, Ontario, Canada during the months of June and July 2019 (See Figure 12b). The exact sampling locations are shown in Fig. 12c. The algae were carefully washed with deionized water to remove sand, salt, and other contaminants attached to their surface. Afterwards, any surplus of water was drained, and the samples were then dried at 105 °C in a furnace overnight. The dried algae were then ground and mixed to ensure uniform consistency and composition of the batch (Fig. 12d). RAB was prepared using a macro TGA at Bio-Renewable Innovation Lab, University of Guelph, Canada (Fig. 12a). Five grams of green macroalgae (sieved into the particle size <150 µm in diameter) were placed into a reactor consisting of a stainless-steel tube of 175 mm height and 15 mm and then the system was purged by the nitrogen gas before starting the reaction. Afterwards, the purged reactor was inserted inside a Muffle Furnace (Model F48055-60, USA) to heat the pyrolysis reactor. The experiments were performed at a heating rate of 15 °C/min, reaching a temperature of 700 °C. The k-type thermocouple was connected to a data-logger to continuously visualize and record the temperature profile on the computer. RAB was utilized as a start material to synthesize3DFAB and CoTLM.
Synthesis of 3DFAB. Four grams of green macroalgae were mixed with 6 M NaOH and refluxed for 5 hours at 100 °C. The resulting suspension was centrifuged and dried before being placed in the pyrolysis reactor. Afterwards, 3DFAB derived from green macroalgae was synthesized by pyrolysis at 700 °C for 2 h and subsequent reflux with H2SO4 and HNO3 (1:3 by volume) at 80 °C for 6 h.

Synthesis of CoTLM. A suspension composed of 1 g 3DFAB, 100 mL of distilled water, Ammonium Hydroxide as pH adjusters (to set pH at ≈11), and 0.25 g of Co(NO3).6H2O was transferred into a Teflon-lined stainless-steel autoclave and heated at 150 °C for 15 h. The resulting products were centrifuged at 5000 rpm. CoTLM was obtained after being washed with distilled water and ethanol several times.

Figure 12. Schematics of the lab-scale experimental set up of the slow pyrolysis process (a) collection (b) Sampling location/Satellite image (c) Dried uniform algae (d)

Preparation of working electrodes in supercapacitor. A homogeneous mixture composed of synthesized samples (RAB, 3DFAB, or CoTLM), carbon black, graphite, and polytetrafluoroethylene (PTFE) was prepared with the assistance of a few droplets of ethanol. Afterward, the mixture was pressed on a piece of a stainless steel current collector (0.5 cm × 1 cm) under a pressure of 10 M Pa and the amount of active
material for each electrode was ranged from 2-3 mg. To fabricate the asymmetric supercapacitor of 3DFAB//CoTLM, 3DFAB and CoTLM were assembled into an MTI cell as negative and positive electrodes, respectively. In this system, glassy fiber (GFA) was used as a separator and 3M KCl was introduced as an aqueous electrolyte.

Characterization of materials. The morphological characteristics and pore structure were investigated through field emission scanning electron microscopy FESEM (MIRA3 LM, Tuscan) at an acceleration voltage of 15.0 kV. To determine the type and intensity of attached functional groups over synthesized materials, Fourier Transform Infrared (FTIR) spectroscopy (Brand: Bruker ISS-88) was used. New crystallinity phases resulting from reaction and interaction among components were determined by studying the XRD patterns recorded by Xpert MPD diffractometer. Textural properties of RAB, CoTLM, and 3DFAB were analyzed by TriStar II 3020 Version 3.02 through Brunauer Emmett Teller (BET) equation. X-ray photoelectron spectroscopy (XPS) measurement was performed in a Perkin Elmer PHI 6000C ECSA system with monochromatic Al KR (1486.6 eV) irradiation.

Electrochemical Measurement. The electrochemical parameters (CV, CCV, GCD, and EIS) of state-of-the-art electrodes were measured using a three-electrode system comprised of CoTLM (3DFAB or RAB) working electrode, an Ag/AgCl reference electrode, and a graphite rod counter electrode. We implemented the same instruction for determining CV, CCV, and GCD, but in a two-electrode system. All electrochemical data were collected using an Autolab 302N, at 25 °C in 3 M KCl electrolyte.

Conclusions

In summary, we have fabricated a cost-effective ASC using RAB and 3DFAB as negative electrodes and CoTLM as a positive electrode. CoTLM were synthesized by integrating pyrolysis and hydrothermal carbonization methods. XRD, FTIR, and FESEM-EDS analyses confirmed the unique hierarchical architecture and superior surface area of CoTLM, resulting high specific capacitance, and excellent cycling stability. The working potential range of 3DFAB was -0.9–0 V, while that of CoTLM was -0.1–0.9 V. Thus, the cell voltage of this two-electrode combination has extended up to 1.7 V, which is significantly higher than that obtained in symmetric type supercapacitors. The energy density acquired from the
3DFAB//CoTLM ASC device is 54.44 Wh kg\(^{-1}\) with a power density of 800 W kg\(^{-1}\), which is significantly larger than that of the RAB//CoTLM (23.22 Wh kg\(^{-1}\) at a power density of 850 W kg\(^{-1}\)). These values are significantly higher than those reported for cobalt and iron-based composite ASCs.

**Author Contributions:** ON and SP equally contributed in designing and performing the experiments, performing the experimental work, and interpreting the results. HN helped in measuring the electrochemical properties. FD and AD have helped in scientific discussion to revise manuscript. ON wrote the manuscript. Animesh Dutta supervised the group during the entire process of project.

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Figure Legends

Figure 1. Possible mechanism of NaOH activation for the synthesis of 3FAB.

Figure 2. FT-IR spectra (a) and XRD patterns (b) of RAB, 3DFAB, CoTLM

Figure 3. FESEM images of the RAB (a), 3DFAB (b), and CoTLM (c)

Figure 4. N₂ adsorption/desorption isotherm and pore size distributions (BJH) of the RAB, 3DFAB, CoTLM (a), Raman analyses (b)

Figure 5. Electrochemical performance of the RAB, 3DFAB, and CoTLM electrodes. Cyclic voltammograms at 50 mV s⁻¹ (a); Cyclic voltammograms RAB, 3DFAB, and CoTLM at increasing rates from 5 to 100 mV s⁻¹ (b, c, d);

Figure 6. 3D-CCV curves of the RAB, 3DFAB, and CoTLM electrodes measured at a scan rate of 50 mV s⁻¹ (a, b, c), variation of the specific capacitance of the RAB, 3DFAB, and CoTLM electrodes with CCV method as a function of the number of cycles at 50 mV s⁻¹ (d, e, f)

Figure 7. GCD of RAB, 3DFAB, and CoTLM at the current densities rates from 1 to 16 A g⁻¹ (a, b, c); and cyclic performance of the RAB, 3DFAB, and CoTLM electrodes at the current density of 4 A g⁻¹ (d, e, f)

Figure 8. Nyquist plots of the RAB, 3DFAB, and CoTLM electrodes.

Figure 9. CV curves at different scan rates of 3DFAB//CoTLM (a), and charge/discharge curves under different current densities of 3DFAB//CoTLM (b)
Figure 10. 3DFAB//CoTLM asymmetric systems measured at a scan rate of 50 mV s\(^{-1}\) (a), variation of the specific capacitance of the 3DFAB//CoTLM cell with CCV method as a function of the number of cycles at 50 mV s\(^{-1}\) (b)

Figure 11. Cycle performance of 3DFAB//CoTLM electrode at the current density of 4 A g\(^{-1}\) (a), Ragone plot of 3DFAB//CoTLM (b)

Figure 12. Schematics of the lab-scale experimental set up of the slow pyrolysis process (a) collection (b) Sampling location/Satellite image (c) Dried uniform algae (d)

Table Legends

Table 1. EDS analyses of RAB, 3DFAB, and CoTLM prepared from green macroalgae.

Table 2. Calculated Values of \(R_s\), CPE, \(R_{ct}\), \(Z_w\), and \(C_f\) through CNLS Fitting of the Experimental Impedance Spectra Based upon the Proposed Equivalent Circuit
