1. Introduction

As part of ongoing efforts to realize a low-carbon and hydrogen-based society, there is an increasing demand for high-performance electrocatalysts, which are key materials for fuel cells and water electrolysis systems. Although platinum group metals exhibit high catalytic activity, increasing production costs due to resource constraints, limited countries of production, and geopolitical supply issues are threatening their use. Therefore, it is crucial to make substantial changes in resource utilization for the sustainable production of electrochemical catalysts. Herein, the preparation of trifunctional biomass-derived electrocatalysts for the oxygen reduction reaction and oxygen/hydrogen evolution reactions by the pyrolysis of cellulose nanofibers from ascidian tunicates, dried blood meal, and cyanocobalamin is reported. The combination of N, P, FeN₄, and CoN₄ structures incorporated in the carbon network leads to high electrochemical performance comparable with rare-metal-based electrocatalysts and other carbon alloy electrocatalysts. This work provides a possible strategy for fabricating high-capacity energy storage devices from biomass resources such as industrial waste without the need for rare metals or other harmful heavy metals.
defined structure obtained by the pyrolysis of metal–organic frameworks (MOFs) have been developed. However, these electrocatalysts utilize mineral and petroleum resources that are also susceptible to resource depletion and price increases due to geopolitical factors, albeit not to the same degree as rare metals. Furthermore, considering the life cycle assessment for these materials, it is very difficult to control the CO₂ emissions during the manufacturing process. Therefore, it is crucial to make substantial changes in resource utilization for the sustainable production of electrochemical catalysts.

Against this background, we have focused on waste biomass resources. Some previous works have reported the preparation of electrocatalysts from biomass resources. For example, natural resources such as cellulose, chitosan, and so on have been exploited to produce electrocatalysts for the ORR and OER, and hydrogen evolution reaction (HER). Furthermore, some of these were bifunctional electrocatalysts, displaying both ORR and OER activity or both OER and HER activity. However, most of them are limited to catalyzing specific reaction process such as ORR, and multifunctional electrocatalyst is rare. Furthermore, the performances of those electrocatalysts are not enough comparing with other synthetic electrocatalysts from rare metals, metal oxides, and other carbon alloys synthesized from organic molecules. Therefore, high-performance and multifunctional electrocatalyst has been demanded. Recently, we reported ORR electrocatalysts prepared by the pyrolysis of polydopamine-coated cellulose nanocrystals extracted from ascidian tunicates. Cellulose extracted from ascidian tunicates has markedly higher crystallinity than wood-based cellulose and affords a good graphitic carbon structure after pyrolysis. Meanwhile, the polydopamine coating served as a source of N dopants and allowed for the complexation of metal ions. Figure 1a,b presents a schematic illustration of the preparation of biomass-derived carbon alloy electrocatalysts. Figure 1c shows the chemical structure of VB₁₂ alongside a photograph of its aqueous solution. The red color of VB₁₂ can be clearly observed. These three components were mixed and ground with a small amount of water and isopropanol using a mortar and pestle. The resulting slurry was dried at 80 °C on a hot stage to obtain the pyrolysis precursor. From previous research, the pyrolysis temperature should be approximately 900 °C and a CNF:BM ratio of at least 1:9 gives good heteroatom-doped carbon materials for ORR and OER electrocatalysts. Therefore, we selected two mixing ratios of CNF:BM:VB₁₂ = 1:9:0 and CNF:BM:VB₁₂ = 1:9:1. After pyrolysis in an electric oven at 900 °C for 2–3 h, the carbon alloy electrocatalysts were obtained.

As shown in Figure 2, TG analysis revealed that the CNFs underwent multiple stages of weight loss due to the evaporation of water and dehydration of the cellulose hydroxy groups. The pyrolysis of the CNFs started above 400 °C and 10.8% of carbonized CNFs finally remained at 900 °C. By contrast, the BM began to undergo pyrolysis at approximately 300 °C and 26.1% residue remained at 900 °C. Because BM is primarily composed of proteins and lipids, these heteroatom-containing molecules tended to degrade faster than the highly crystalline cellulose of the CNFs. The TG curve for CNF:BM:VB₁₂ = 1:9:0 was almost identical to that for the BM, which was the major component of the former sample, and the final amount of residue was 23.5%. This slightly higher weight loss was attributable to the presence of 10% of the CNFs, which underwent greater weight loss during pyrolysis compared with the BM as described above. The TG curve for CNF:BM:VB₁₂ = 1:9:1 was also almost identical to that for the BM, although the amount of residue remaining after pyrolysis was slightly higher owing to the complexed VB₁₂.

XPS spectra were recorded to confirm the incorporation of heteroatoms in the pyrolyzed biomass samples. Figure 3 shows the XPS spectra for CNF:BM:VB₁₂ = 1:9:0 and CNF:BM:VB₁₂ = 1:9:1. From the wide-scan spectra shown in Figure 3a, peaks corresponding to C 1s, N 1s, O 1s, and O KLL were clearly observed. In addition, a Ca 2p peak was detected at 345 eV, which was ascribed to a small amount of Ca ion impurities in the CNFs derived from the seashells used as scaffolds during ascidian culture. A trace amount of these impurities apparently remained in the samples after the several washing steps used to purify the CNFs. Figure 3b shows the narrow-scan XPS spectra for C 1s. For both samples, intense peaks corresponding to C–C and C=O were observed at 284 eV. In addition, shoulders corresponding to C–N bonds were detected at approximately 296 eV, which implies N doping into the carbon networks. As shown in Figure 3c, peaks corresponding to P 2p were found at 133 eV.
for both samples. Figure 3d shows the narrow-scan XPS spectra for N 1s. Because the original signals were noisy, smoothed lines were obtained using a lowess filter (red and blue lines). These lines indicated the presence of both pyrrolic and pyridinic N atoms, which are well known to serve as efficient catalytic centers for the ORR. Because the pyrrole moieties of hemoglobin were originally complexed to Fe in the dried BM, the signals corresponding to pyrrolic N atoms also support the incorporation of the FeN₄ structure into the carbon network. [41] Furthermore, the relative intensity of the peak corresponding to pyrrolic N atoms increased in the case of CNF:BM:VB₁₂ = 1:9:1 owing to the presence of pyrrole moieties in VB₁₂. Figure 3e,f shows the narrow-scan XPS spectra for Fe 2p and Co 2p, respectively. In the former spectra, the smoothed lines indicated the presence of spin states of 1/2 and 3/2 for both Fe²⁺ and Fe³⁺, in accordance with the coexistence of both Fe(II) and Fe(III). In the latter spectrum, similar peaks for Co 2p₁/₂ and Co 2p₃/₂ were observed in the case of CNF:BM:VB₁₂ = 1:9:1. [42] These results indicate that FeN₄ from hemoglobin was successfully incorporated into the carbon network in the case of CNF:BM:VB₁₂ = 1:9:0, while both FeN₄ from hemoglobin and CoN₄ from VB₁₂ were incorporated into the carbon network in the case of CNF:BM:VB₁₂ = 1:9:1. The incorporation of Co in the pyrolyzed CNF:BM:VB₁₂ = 1:9:1 was also confirmed by transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDX) (see S1, Supporting Information).

Figure 4a,b shows the Raman spectra of pyrolyzed CNF:BM:VB₁₂ = 1:9:0 and pyrolyzed CNF:BM:VB₁₂ = 1:9:1, respectively, in the range of 1000–2000 cm⁻¹. Clear defect (D) and graphitic...
(G) bands can be observed. In the case of CNF:BM:VB12 = 1:9:0, the peak areas of the D and G bands were almost identical with a D/G ratio of 1.26, which is close to that for typical carbon black materials. By contrast, the Raman spectrum of CNF:BM:VB12 = 1:9:1 revealed a broad D band and a D/G ratio of 2.08. This indicates a larger number of defects in the obtained carbon surface, which was ascribed to the incorporation of CoN4 structures from VB12 in accordance with the XPS analysis results.

3. ORR and OER Performance

Figure 5a presents the LSV curves for GC, Pt/C, CNF:BM:VB12 = 1:9:0, and CNF:BM:VB12 = 1:9:1 in the range of 0.2–1.1 V versus RHE, which corresponds to the region where the ORR occurs. The corresponding electrochemical performance parameters are summarized in Table 1. As shown in the plot, GC displayed a low onset potential ($E_{\text{onset}}$), whereas Pt/C showed a high $E_{\text{onset}}$ of 1.056 V versus RHE for the ORR. The half-wave potential ($E_{1/2}$) for Pt/C was 0.870 V versus RHE. The combination of the CNFs and BM greatly improved the ORR performance compared with GC, as demonstrated by the $E_{\text{onset}}$ and $E_{1/2}$ values of 0.943 and 0.808 V versus RHE, respectively. Although these values are lower than those obtained for Pt/C, they are high compared with other biomass-derived electrocatalysts. The ORR performance of CNF:BM:VB12 = 1:9:1 was slightly superior to that of CNF:BM:VB12 = 1:9:0 ($E_{\text{onset}} = 0.983$ V vs RHE, $E_{1/2} = 0.864$ V vs RHE) because the CoN4 structure also possesses ORR activity.

It is well known that the ORR typically proceeds via one of two reduction processes, namely, a two-electron process in which O2 is converted into H2O2 or a four-electron process in which OH− is directly generated from O2. The four-electron process is an ideal process of ORR, leading to high demand for electrocatalysts that mediate this process. Figure 5b shows the calculated electron numbers ($n$) obtained using Equation (3) and the H2O2 ratios for Pt/C (orange lines), CNF:BM:VB12 = 1:9:0 (blue lines), and CNF:BM:VB12 = 1:9:1 (red lines). In the case of Pt/C, $n$ remained close to 4.0 and the H2O2 ratio was less than 1%, indicating an almost ideal four-electron process for this catalyst. By contrast, the $n$ values for CNF:BM:VB12 = 1:9:0 and CNF:BM:VB12 = 1:9:1 ranged from 3.5 to 3.7, while the H2O2 ratio surpassed 5% for the former catalyst. Thus, the two developed electrocatalysts displayed ORR performance that was promising, albeit slightly lower than that of Pt/C.

Figure 5c shows a Tafel plot for Pt/C, CNF:BM:VB12 = 1:9:0, and CNF:BM:VB12 = 1:9:1, which provided insights into the rate-limiting step of the ORR. There are several possible rate-limiting steps in the ORR, such as the protonation of superoxide ($O_2^-$)
and the adsorption of O\textsubscript{2} molecules onto active sites.\textsuperscript{[44]} It has reported that following four rate-limiting steps existing and corresponding Tafel slope values were reported.

\[
\begin{align*}
\text{O}_2 + C & \rightarrow \text{OOH}^\cdot (120 \text{ mV dec}^{-1}) \\
\text{OOH}^\cdot + e^- & \rightarrow \text{O}^\cdot + \text{OH}^\cdot (60 \text{ mV dec}^{-1}) \\
\text{O}^\cdot + C & \rightarrow \text{OH}^\cdot (24 \text{ mV dec}^{-1}) \\
2(\text{OH}^\cdot + C) & \rightarrow \text{H}_2\text{O}^\cdot + \text{H}_2\text{O}^\cdot (40 \text{ mV dec}^{-1})
\end{align*}
\]

Figure 4. Raman spectra of a) pyrolyzed CNF:BM:VB\textsubscript{12} = 1:9:0 and b) pyrolyzed CNF:BM:VB\textsubscript{12} = 1:9:1. The black lines show the actual spectra and the green lines show the waveform separation of each peak. The red lines show integral of green lines. The D/G values were calculated from the corresponding peak areas.

The asterisk shows adsorbed species on the active site of electrocatalysts. The Tafel slope for Pt/C was 50 mV dec\textsuperscript{-1}, indicating that the rate-limiting steps of the ORR on this catalyst were around (2) and (4). The Tafel slopes for CNF:BM:VB\textsubscript{12} = 1:9:0 and CNF:BM:VB\textsubscript{12} = 1:9:1 were 49 and 39 mV dec\textsuperscript{-1}, respectively. From those values, CNF:BM:VB\textsubscript{12} = 1:9:0 shows same rate limiting step as Pt/C but the rate-limiting step of CNF:BM:VB\textsubscript{12} = 1:9:1 was mainly (4).\textsuperscript{[45]}

Figure 5d,e show the kinetic ORR performance for CNF:BM:VB\textsubscript{12} = 1:9:0 and CNF:BM:VB\textsubscript{12} = 1:9:1, respectively. In the case of CNF:BM:VB\textsubscript{12} = 1:9:0, \(E_{\text{onset}}\) gradually decreased with increasing rotational speed of the electrode, whereas \(E_{\text{onset}}\) remained constant for CNF:BM:VB\textsubscript{12} = 1:9:1. Figure 5f,g present the corresponding K–L plots, which were used to calculate the \(n\) values from the LSV curves. \(J_k\) values of CNF:BM:VB\textsubscript{12} = 1:9:0 and CNF:BM:VB\textsubscript{12} = 1:9:1 were both 3.94 mA cm\textsuperscript{-2} at 0.5 V vs RHE in the LSV slopes at 1,600 rpm. In the case of CNF:BM:VB\textsubscript{12} = 1:9:0, the \(n\) values ranged from 3.50 to 3.75. These increased to 3.74–3.81 for CNF:BM:VB\textsubscript{12} = 1:9:1. These results are in good agreement with the \(n\) values calculated from Equation (3) as plotted in Figure 5b.

The OER performance of the electrocatalysts was evaluated by using the potential at \(J = 10 \text{ mA cm}^{-2}\) \((E_j = 10 \text{ mA cm}^{-2})\). As shown in Figure 6a, the value of \(E_j = 10 \text{ mA cm}^{-2}\) for Pt/C was found to be 2.057 V versus RHE. By contrast, pyrolyzed CNF:BM:VB\textsubscript{12} = 1:9:0 and CNF:BM:VB\textsubscript{12} = 1:9:1 exhibited superior OER performance, with \(E_j = 10 \text{ mA cm}^{-2}\) values of 1.884 and 1.726 V versus RHE, respectively.

It is well known that Fe\textsubscript{N} and Co\textsubscript{N} contribute to enhancing both the ORR and OER performance. For example, Duan et al. reported the preparation of MOF-derived Fe, Co, and N doped carbon bifunctional electrocatalysts and demonstrated the synergetic effect of Fe\textsubscript{N} and Co\textsubscript{N} on the ORR and OER.\textsuperscript{[46]} Density functional theory calculations revealed that the adsorption energies of the intermediates played a critical role in the catalytic performance. In the case of OH\textsuperscript{−}, the adsorption energy was low for Co centers, high for Fe centers, and intermediate for Fe–Co double centers. These differences occurred because the interaction between Fe and Co altered the electronic state distribution of the two central metal atoms, ultimately leading to high ORR and OER activity for the bimetallic catalysts.

In alkaline solution, the OER mechanism generally begins with electron transfer to the metal site, followed by consecutive reaction steps that convert OH\textsuperscript{−} to O\textsubscript{2}, where the value of the Tafel slope provides crucial information regarding the rate-limiting step. Figure 6b shows the Tafel plot for Pt/C, CNF:BM:VB\textsubscript{12} = 1:9:0, and CNF:BM:VB\textsubscript{12} = 1:9:1. The Tafel slope for Pt/C was 125 mV\textsuperscript{-1}dec, suggesting that the rate of the OER process was controlled by the initial stage of the reaction, where the catalyst binds hydroxy groups with concomitant electron transfer.\textsuperscript{[47,48]} The Tafel slope for CNF:BM:VB\textsubscript{12} = 1:9:0 was similar to that for Pt/C, indicating that the rate-limiting step was the same. By contrast, the Tafel slope for CNF:BM:VB\textsubscript{12} = 1:9:1 was 59 mV dec\textsuperscript{-1}, which is much lower than those of the two aforementioned electrocatalysts, suggesting that in this case the OER process was limited instead by the O–O bond formation reaction.\textsuperscript{[49]}

Figure 6c shows a combined plot of the LSV curves for all samples in both the ORR and OER regions. The parameter \(\Delta E = E_j = 10 \text{ mA cm}^{-2} – E_{1/2}\) was used as an indicator of the electrochemical performance of the bifunctional ORR and OER electrocatalysts. The \(\Delta E\) values for Pt/C, CNF:BM:VB\textsubscript{12} = 1:9:0, and CNF:BM:VB\textsubscript{12} = 1:9:1 were found to be 1,187, 1,076, and 862 mV, respectively. This \(\Delta E\) value for CNF:BM:VB\textsubscript{12} = 1:9:1 is far superior to those of previously reported N-doped carbons (≈1000 mV) and comparable with synthetic heteroatom-doped carbon materials (800–1000 mV). It should be emphasized that this high electrocatalytic performance was realized solely using biomass resources without any petrochemical products or rare metals.
Figure 5. a) LSV curves for GC (black), Pt/C (orange), CNF:BM:VB12 = 1:9:0 (blue), and CNF:BM:VB12 = 1:9:1 (red) in the range of 0.2–1.1 V versus RHE, which corresponds to the region where the ORR occurs. b) Calculated $n$ values and H$_2$O$_2$ ratios for Pt/C (orange), CNF:BM:VB12 = 1:9:0 (blue), and CNF:BM:VB12 = 1:9:1 (red). c) Tafel plot for Pt/C. CNF:BM:VB12 = 1:9:0, and CNF:BM:VB12 = 1:9:1. d,e) Kinetic LSV curves for (d) CNF:BM:VB12 = 1:9:0 and (e) CNF:BM:VB12 = 1:9:1 upon varying the rotational speed of the electrode from 400 to 3,200 rpm. f,g) K–L plots calculated from the kinetic LSV curves for (f) CNF:BM:VB12 = 1:9:0 and (g) CNF:BM:VB12 = 1:9:1.

Table 1. Electrochemical performance parameters for the samples used in this study.

| Sample             | $C_{CNF}$ [%] | $C_{BM}$ [%] | $C_{VB12}$ [%] | ORR $E_{onset}$ [V vs RHE] | ORR $E_{1/2}$ [V vs RHE] | OER $E_{onset}$ [V vs RHE] | OER $E_{1/2}$ [V vs RHE] | $\Delta E$ [mV] | HER $E_{onset}$ [V vs RHE] | HER $E_{1/2}$ [V vs RHE] |
|--------------------|---------------|--------------|---------------|--------------------------|--------------------------|--------------------------|--------------------------|----------------|--------------------------|--------------------------|
| CNF:BM:VB12 = 1:9:0| 10            | 90           | 0             | 0.943                    | 0.808                    | 1.884                    | 1.076                    | 0.943          | 0.808                    | 1.884                    |
| CNF:BM:VB12 = 1:9:1| 9             | 82           | 9             | 0.983                    | 0.864                    | 1.726                    | 0.972                    | 1.726          | 0.972                    | 1.726                    |
| Pt/C               | –             | –            | –             | 1.056                    | 0.870                    | 2.057                    | 1.187                    | 0.241          | 0.241                    | 0.241                    |
| GC                 | –             | –            | –             | 0.781                    | 0.640                    | –                        | –                        | –              | –                        | –                        |

Figure 6. a) LSV curves for GC (black), Pt/C (orange), CNF:BM:VB12 = 1:9:0 (blue), and CNF:BM:VB12 = 1:9:1 (red) in the range of 1.2–2.1 V versus RHE, which corresponds to the region where the OER occurs. b) Tafel plot for Pt/C. CNF:BM:VB12 = 1:9:0, and CNF:BM:VB12 = 1:9:1. c) Combined plot of the LSV curves for all samples in both the ORR and OER regions.
H₂ molecule can be released from the catalyst surface via either diate and OH⁻ on an active site on the catalyst surface to form a M⁻ adsorbed hydrogen, respectively. Initially, hydrogen is adsorbed RHE. Compared with GC, CNF:BM:VB₁₂⁻¹ displayed higher HER activity close to that of Pt/C. According to the literature, the Tafel slope varies with the rate-determining step for the HER in alkaline media as follows[50]

\[
\text{Volmer step: } \text{H}_2 \text{O} + \text{M}^+ + \text{e}^- \rightleftharpoons \text{M}^- + \text{OH}^- (120 \text{ mV dec}^{-1})
\]

\[
\text{Heyrovsky step: } \text{H}_2 \text{O} + \text{M}^- + \text{H}^+ + \text{e}^- \rightleftharpoons \text{M} + \text{H}_2 + \text{OH}^- (40 \text{ mV dec}^{-1})
\]

\[
\text{Tafel step: } \text{M}^- + \text{M}^- + \text{H}^+ \rightleftharpoons \text{M} + \text{H}_2 (30 \text{ mV dec}^{-1})
\]

In the above equations, M and H denote an active site and adsorbed hydrogen, respectively. Initially, hydrogen is adsorbed on an active site on the catalyst surface to form a M–H intermediate and OH⁻ in the Volmer adsorption step. Subsequently, a H₂ molecule can be released from the catalyst surface via either the Heyrovsky step or the Tafel step. In the case of Pt/C, the Tafel slope was 60.5 mV dec⁻¹, which indicates that the H₂ molecules were released from M–H via the Heyrovsky step and this was the rate-limiting step. By contrast, the Tafel slopes for CNF:BM: VB₁₂⁻¹ and CNF:BM:VB₁₂⁻¹ were 118 and 92.7 mV dec⁻¹, respectively, which indicates that hydrogen adsorption (i.e., the Volmer step) was the rate-limiting step for these electrocatalysts.

4. HER Performance

In addition to the ORR and OER characteristics, the HER performance was evaluated. Figure 7a shows the LSV curves for the four samples in the range from −1.0 to 0.4 V versus RHE, which corresponds to the region where the HER occurs. Because Pt/C exhibits its good HER properties, the E_onset was approximately 0 V versus RHE. Compared with GC, CNF:BM:VB₁₂⁻¹ and CNF:BM: VB₁₂⁻¹ displayed higher HER activity close to that of Pt/C.

Figure 7b shows the corresponding Tafel plot for GC, CNF:BM:VB₁₂⁻¹, and CNF:BM:VB₁₂⁻¹. According to the literature, the Tafel slope varies with the rate-determining step for the HER in alkaline media as follows[50]

\[
\text{Volmer step: } \text{H}_2 \text{O} + \text{M}^+ + \text{e}^- \rightleftharpoons \text{M}^- + \text{OH}^- (120 \text{ mV dec}^{-1})
\]

\[
\text{Heyrovsky step: } \text{H}_2 \text{O} + \text{M}^- + \text{H}^+ + \text{e}^- \rightleftharpoons \text{M} + \text{H}_2 + \text{OH}^- (40 \text{ mV dec}^{-1})
\]

\[
\text{Tafel step: } \text{M}^- + \text{M}^- + \text{H}^+ \rightleftharpoons \text{M} + \text{H}_2 (30 \text{ mV dec}^{-1})
\]

In the above equations, M and H denote an active site and adsorbed hydrogen, respectively. Initially, hydrogen is adsorbed on an active site on the catalyst surface to form a M–H intermediate and OH⁻ in the Volmer adsorption step. Subsequently, a H₂ molecule can be released from the catalyst surface via either the Heyrovsky step or the Tafel step. In the case of Pt/C, the Tafel slope was 60.5 mV dec⁻¹, which indicates that the H₂ molecules were released from M–H via the Heyrovsky step and this was the rate-limiting step. By contrast, the Tafel slopes for CNF:BM: VB₁₂⁻¹ and CNF:BM:VB₁₂⁻¹ were 118 and 92.7 mV dec⁻¹, respectively, which indicates that hydrogen adsorption (i.e., the Volmer step) was the rate-limiting step for these electrocatalysts.

5. Conclusion

We have developed a trifunctional and rare-metal-free electrocatalyst for the ORR, OER, and HER that can be synthesized entirely from biomass resources by simple pyrolysis. The combination of N, P, FeN₄, and CoN₄ structures incorporated in the carbon network led to high electrochemical performance comparable with rare-metal-based electrocatalysts and other carbon alloy electrocatalysts. This work provides a possible strategy for fabricating high-capacity energy storage devices from biomass resources such as industrial waste without the need for rare metals or other harmful heavy metals. We believe that the obtained results represent a giant step forward for realizing a low-carbon sustainable society and circular economy.

6. Experimental Section

Materials: CNFs were extracted from ascidian tunicates and purified according to the literature[51] Ascidian tunicates were crushed in a biaxial-type shear crusher (Ujije, Japan) and the residual seashell material used as a scaffold during ascidian culture was removed by washing with water. After drying, the material was milled at 18 500 rpm for 10 min with a mechanical mixer (FMI, Japan) and treated at 12% w/w solution of sodium hypochlorite (NaClO) at room temperature for 24 hrs. The dispersion was dispersed by fine grinding using mechanical homogenizer (Microtech Nichion, Japan) equipped with a 20 mm-diameter shaft at 7500 rpm for 5 min and concentrated by centrifugation to prepare 2 wt% dispersion. Dried blood meal (BM) was kindly provided by Tomikura Sangyo (Himeji, Japan). Vitamin B₁₂ (VB₁₂, cyanocobalamin) and 2% NaClO were purchased from Sigma-Aldrich (St. Louis, MO). Isopropanol (IPA, GR) was purchased from Fujifilm Wako Co. Ltd. (Japan). Cu foil was purchased from Nira Co., Ltd., Japan. 20 wt% Pt/C catalyst was purchased from Sigma-Aldrich, St. Louis, MO.

Electrocatalyst Preparation: The samples used in this study are listed in Table 1. The purified CNFs, BM, and VB₁₂ were mixed in a ratio of 1:9:1 or 1:9:0 w/w/w and suspended in a small amount of water and isopropanol then ground. The resulting pastes were dried at 80 °C for 3 h and then placed on pieces of Cu foil and pyrolyzed at 900 °C for 2–3 h in an electric oven (VF-5000, SK Medical Electronics, Co. Ltd., Nagahama, Japan. After
cooling down to room temperature, the carbonized specimens were obtained.

**Characterization:** XPS was conducted on a JPS9200 spectrometer (JEOL; Al Kα, 10 kV, 10–15 mA). Wide scans were performed from 0 to 1400 eV in 1 eV steps, and narrow scans for each element were performed in 0.1 eV steps. Thermogravimetric (TG) analysis was performed on a Thermo Plus Evo 2 TD system (Rigaku, Tokyo). The sample was placed in a Pt crucible and the temperature was increased from room temperature to 1000 °C at a rate of 10 °C min⁻¹ under N₂ flow. Raman spectroscopy was conducted on a LabRAM HR-800 instrument (Horiba, Japan) with 532 nm laser excitation to determine the quality of the carbon networks in the pyrolyzed samples. Scanning electron microscopy (SEM) images were obtained by using an S-5200, Hitachi-Hitechnologies, Japan.

**Evaluation of Electrochemical Performance:** The ORR, OER, and HER performance was evaluated by linear sweep voltammetry (LSV) measurements using a potentiostat (2325, BAS, Japan) according to a previous study.[51] For each sample, a catalyst ink was prepared by dispersing the catalyst (0.82 mg) in a solution (1 mL) consisting of Na₂CO₃ (Sigma-Aldrich), isopropanol (334 μL), and water (84 μL) with sonication for 5 min. The catalyst ink (20 μL) was then cast onto the glassy carbon (GC) insert (BAS, Japan) of a rotating ring-disc electrode (RRDE, 4 mm diameter, BAS, Japan, both ring and disk electrodes has 0.126 cm² surface area) and dried. The catalyst loading on the electrode was 300 μg cm⁻². A Pt wire and an Ag/AgCl electrode were inserted into the electrolyte as the counter and reference electrodes, respectively. A 0.1 M KOH solution bubbled with N₂ or O₂ for 30 min was used as the electrolyte.

The potential versus Ag/AgCl was converted to the reversible hydrogen electrode (RHE) scale using the following equation

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059V - \text{pH}$$

The number of electrons (n) involved in the ORR was calculated according to the Koutecký–Levich (K–L) equation[52,53]

$$J = \frac{1}{J_k} = \frac{1}{J_n} = \frac{D_O^2 \nu C_{O_2}^{0.5}}{\nu C_{O_2}^{0.5} + 0.62 n F A D_O^2 C_{O_2}^{\frac{1}{2}}}, \frac{1}{k F A C_{O_2}^{0.5}}$$

where $J$, $J_n$, and $J_k$ are the measured, kinetic, and diffusion-limited current, respectively, $F$ is the Faraday constant (96 485 C mol⁻¹); $A$ is the electrode area (0.1256 cm²); $k$ is the rate constant for oxygen reduction (M s⁻¹); $D_O$ is the diffusion coefficient of O₂ in the electrolyte (1.9 × 10⁻⁵ cm² s⁻¹); $\nu$ is the viscosity of the electrolyte solution (0.01 cm² s⁻¹); $C_{O_2}^{0.5}$ is the saturated concentration of O₂ in the electrolyte (1.2 × 10⁻⁸ mol cm⁻³); and $\omega$ is the angular rotation rate.[54,55]

The number of electrons (n) involved in the ORR was also calculated using the RRDE results and the following equation[56]

$$n = \frac{4 I_n}{I_D}$$

where $I_D$ and $I_n$ are the current densities for the disk and ring electrodes, respectively, and $N$ is the capture efficiency (0.42).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

biomass, cellulose nanofibers, electrocatalysts, hydrogen evolution reactions, oxygen evolution reactions, oxygen reduction reactions, vitamin B₁₂

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