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Carbon nanotube dispersed conductive network for microbial fuel cells

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Microbial fuel cells (MFCs) are promising devices for capturing biomass energy. Although they have recently attracted considerable attention, their power densities are too low for practical use. Increasing their electrode surface area is a key factor for improving the performance of MFC. Carbon nanotubes (CNTs), which have excellent electrical conductivity and extremely high specific surface area, are promising materials for electrodes. However, CNTs are insoluble in aqueous solution because of their strong intertube van der Waals interactions, which makes practical use of CNTs difficult. In this study, we revealed that CNTs have a strong interaction with *Saccharomyces cerevisiae* cells. CNTs attach to the cells and are dispersed in a mixture of water and *S. cerevisiae*, forming a three-dimensional CNT conductive network. Compared with a conventional two-dimensional electrode, such as carbon paper, the three-dimensional conductive network has a much larger surface area. By applying this conductive network to MFCs as an anode electrode, power density is increased to $176 \mu\text{W}/\text{cm}^2$, which is approximately 29-fold higher than that in the case without CNTs addition. Maximum current density is also increased to approximately 16-fold higher. These results suggest that three-dimensional CNT conductive network contribute to improve the performance of MFC by increasing surface area.

Microbial fuel cells (MFCs), which have generated considerable interest among academic researchers, are emerging devices that generate electricity through microbial catabolic activity.¹⁻⁴ In these devices, microorganisms stored in the anode chamber break down and

oxidize organic matter into carbon dioxide. These processes generate electrons that migrate towards the cathode. At the same time, protons released from the microorganisms pass through a proton exchange membrane (PEM) and penetrate into the cathode chamber. The electrons are drawn via a circuit from the anode to the cathode, where they combine with hydrogen ions and the ambient oxygen to form water. MFCs can generate electricity from various materials, including complex organic waste and renewable biomass. This is why MFCs are also expected to be used in wastewater treatment facilities. By employing a renewable biomass as fuel, there is no net carbon emission because the exhausted carbon dioxide originates from the atmosphere through photosynthesis. However, MFCs have too low power densities to be competitive with conventional chemical fuel cells. One method of improving the power densities of MFCs is to increase the electrode surface area.⁵⁻⁶ To this end, we focused on the usage of CNTs.

CNTs, discovered in 1991,⁷ are suitable materials for electrodes because they are cylindrical with an extremely high specific surface area and an excellent electrical conductivity. However, they are sparsely dispersed in aqueous solutions because of their strong intertube van der Waals interactions, which makes their practical use difficult.⁸

In this study, we revealed that CNTs have a strong interaction with the microorganism *Saccharomyces cerevisiae*. Figure 1 shows an environmental scanning electron microscopy (SEM) image of CNTs and *S. cerevisiae*. As shown in Fig. 1, *S. cerevisiae* cells attach to CNTs. Moreover, CNTs are dispersed in a mixture of water and *S. cerevisiae* cells. In order to fix an *S. cerevisiae* cell, osmication was conducted before SEM observations. The CNTs utilized in the SEM observation (VGNF, Showa Denko) were synthesized by chemical vapor deposition (CVD) method. The diameter and length of the CNTs were 80 nm and 20 μm , respectively.

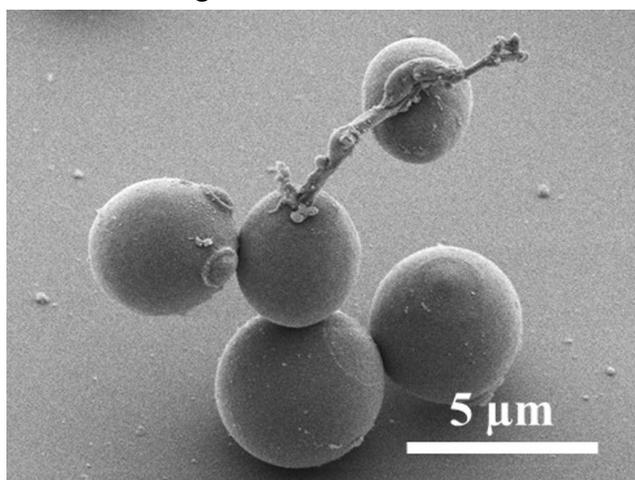


FIG. 1. Scanning electron microscopy image of CNTs and *S. cerevisiae*.

By using the interaction between CNTs and *S. cerevisiae*, we developed a three-dimensional conductive network of dispersed CNTs. This 3D conductive network is formed in the anode solution. Figure 2 shows a schematic of the 3D conductive network. Compared with a conventional 2D electrode, such as carbon paper or a graphite plate,⁹ the 3D conductive

network has a very large surface area and makes the most of the entire space of the anode chamber. Through this 3D conductive network, electrons released from the microorganisms are collected efficiently. By dispersing CNTs into the anode solution directly, CNTs come into contact with each other and form a 3D random network. At this point, *S. cerevisiae* can act not only as a biocatalyst¹⁰ but also as a CNT dispersant. Therefore, CNTs can disperse in the anode solution without any additional processes, such as surface modification¹¹ and the use of a chemical dispersant.¹²

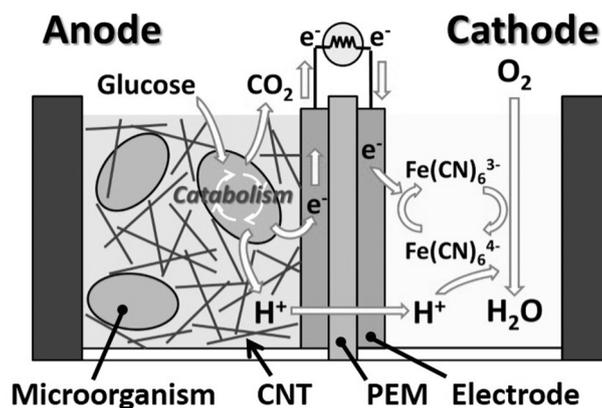


FIG. 2. Schematic of three-dimensional conductive network of dispersed CNTs.

A double-chamber MFC, which had two chambers (anode and cathode chambers) separated by a PEM (Neosepta, CMX, ASTOM), was employed as the reactor cell. Each chamber had a volume of 10 cm³. Carbon paper (3.0×3.0 cm², TGP-H-090, Toray) was employed as both the anode and cathode. The pHs of the anode and cathode solutions were adjusted to 7.0 using 0.3 M phosphate buffer. The anode solution contains 50 g/L *S. cerevisiae*, 30 g/L glucose and 1.0 mM methylene blue, which acts as an electron mediator.¹³ The electron mediator enhances the electron transfer from inside the microorganisms to the anode. 0.1 M ferricyanic potassium was utilized as an oxidant to assist the redox reaction at the cathode. During a measurement, the reactor cell was placed in a constant temperature bath kept at 35 deg C.

Firstly, vapor - grown carbon fibers (VGCFs, Showa Denko), whose diameter and length were 150 nm and 10 μm, respectively, were dispersed in the anode solution at a concentration of 0.1 wt.% to 1.0 wt.%, and the electrochemical characteristics of the MFC cell were measured with a potentiostat (HAL-3001, Hokuto Denko). VGCFs were added to the anode solution directly, followed by steering for 15 min. Figure 3 shows current-voltage and current-power curves in the cases with and without VGCFs. As shown in Fig. 3, in the case with 0.1 wt.% VGCFs, there were small increases in maximum current density and maximum power density, compared with the case without VGCFs. Also, in the case with 0.5 wt.% VGCFs, the maximum current and power densities did not increase markedly. On the other hand, in the case with 1.0 wt.% VGCFs, the maximum current and power densities increased to 230 μA/cm² and 46 μW/cm²,

respectively. Both the maximum current and power densities increased with increasing VGCF concentration, indicating that the 3D conductive network of dispersed VGCFs is easily formed when the VGCF concentration is high.

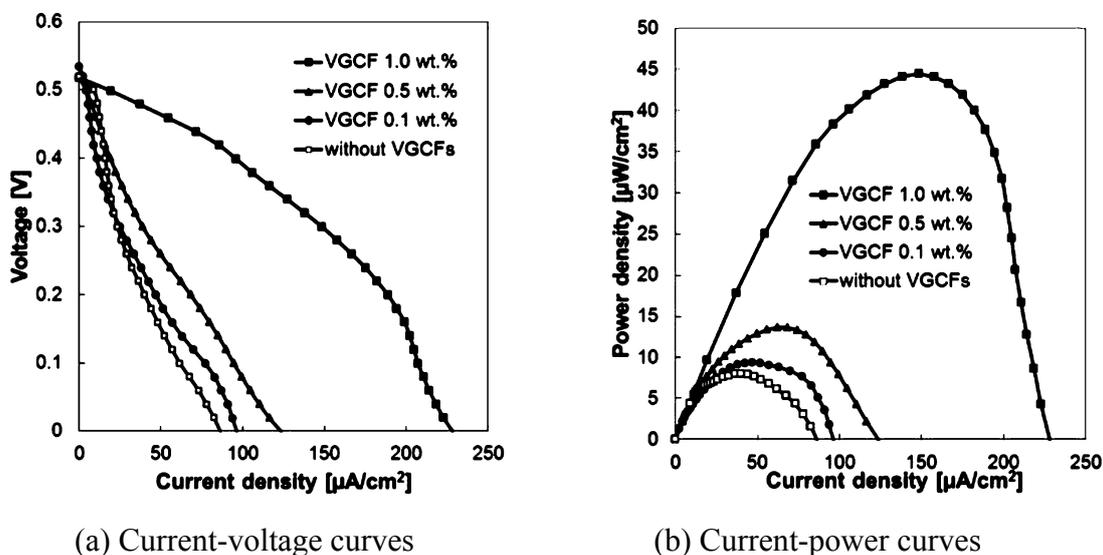


FIG. 3. Current-voltage and current-power curves in cases with and without VGCFs.

Secondly, cyclic voltammograms (CVs) of the anode solution were obtained with a HZ-5000 system (Hokuto Denko) by a three-electrode method. Carbon paper used as the MFC anode and cathode was employed as the working electrode. Ag/AgCl and Pt electrodes were employed as the reference and counter electrodes, respectively. All measurements were conducted at 35 deg C. Figure 4 shows the CVs in the cases with and without 1.0 wt.% VGCFs at a scan rate of 5mV/s from -400 mV to 100 mV (*vs* Ag/AgCl). In the case without VGCFs, an anode peak current of 1.4 mA was observed at -132 mV and a cathode peak current of -0.2 mA was observed at -186 mV. At the same time, in the case with 1.0 wt.% VGCFs, an anode peak current of 3.3 mA was observed at -120 mV and a cathode peak current of -1.2 mA was observed at -196 mV. The anode and cathode peak potentials did not shift significantly, and both the anode and cathode peak currents increased with the addition of VGCFs. The CVs correspond to the current-voltage and current-power curves shown in Fig. 3, indicating that a 3D conductive network of dispersed VGCFs was formed and the surface area of the anode increased.

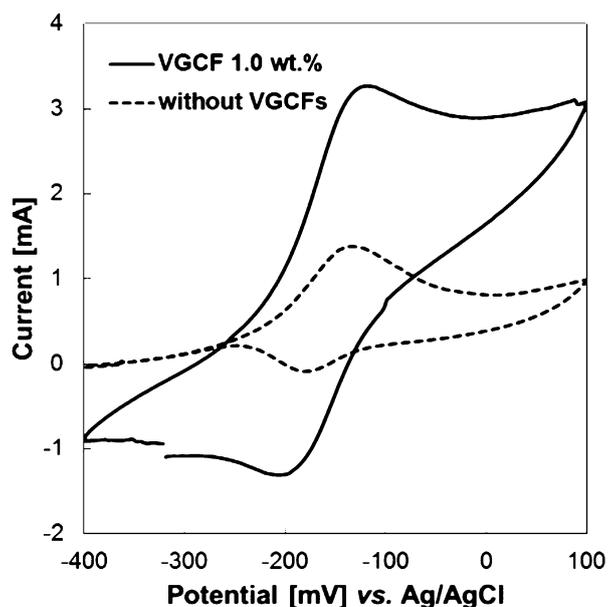


FIG. 4. Cyclic voltammograms in cases with and without 1.0 wt.% VGCFs at a scan rate of 5mV/s.

Thirdly, the SEM observation of the anode solution was conducted. Figure 5 shows a SEM image of the anode solution containing VGCFs at a concentration of 1 wt.%. VGCFs attach to the *S. cerevisiae* cells or to each other, forming the 3D conductive network of dispersed VGCFs. This 3D conductive network contributed to the increase in anode surface area and the improvement of the MFC performance.

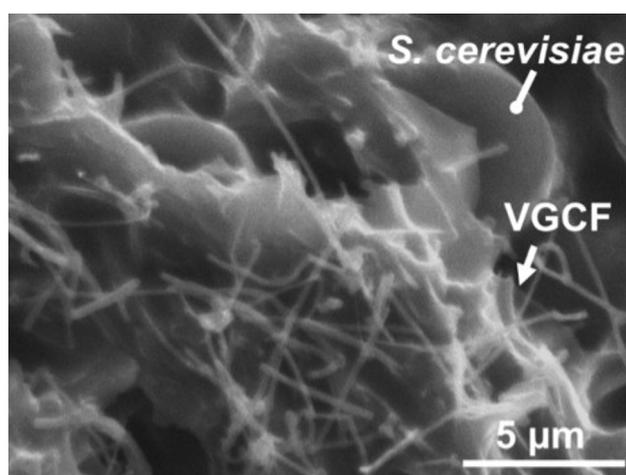


FIG. 5. Scanning electron microscopy image of anode solution.

These results can be explained by the percolation theory.¹⁴⁻¹⁶ Dynamic percolation is the phenomenon that when the volume fraction of CNTs dispersed in the solution exceeds a certain threshold, CNTs attach to each other and form a conductive network of CNTs. The theoretical

percolation threshold is given by Eq. (1), where ϕ_c is the critical volume fraction, P is the dispersion index, γ_C and γ_P are the surface energy density of CNTs and that of the solution, respectively, Δg^* is the critical energy obtained from experimental results, R is the CNT radius, and L is the CNT length. In the Eq. (1), assuming that $P = 1$ and γ_C , γ_P and Δg^* are constant, thinner and longer CNTs are suitable for forming the conductive network.

$$\phi_c = \left\{ \left[1 + \frac{2P(\gamma_C + \gamma_P - 2\gamma_C^{0.5}\gamma_P^{0.5})}{\Delta g^*} \right] \left(\frac{R + L}{RL} \right) \right\}^{-1} \quad (1)$$

Therefore, we synthesized thin and long CNTs suitable for microbial fuel cells by a thermal CVD method, in which toluene and ferrocene were utilized as the carbon source and catalyst, respectively.¹⁷ The synthesis time was 5 h and the synthesis temperature was 760 deg C. The average diameter and length of the synthesized CNTs were 40 nm and 1.5 mm, respectively. Figure 6 shows the Raman spectrum of synthesized CNTs. The Raman spectrum exhibits G- and D-peaks at approximately 1580 and 1350 cm^{-1} , respectively.¹⁸ I_D/I_G was 0.21, indicating that the CNTs include a certain amount of disorder in their sp^2 chains.

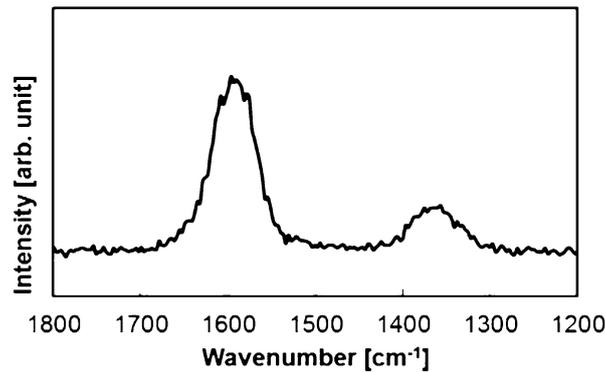


FIG. 6. Raman spectrum of synthesized CNTs.

Finally, the synthesized CNTs were dispersed in the anode solution at a concentration of 0.5 wt.% and the cell performance was tested. All the experimental conditions were the same as those indicated above. Figure 7 shows current-voltage and current-power curves in cases with and without the synthesized CNTs. As expected, the maximum current density increased approximately 16-fold, which indicates that the electrode surface area markedly increased with the addition of CNTs. At the same time, the maximum power density increased to 176 $\mu\text{W}/\text{cm}^2$, which is approximately 29-fold higher than that in the case without CNTs. Figure 7 also shows that the internal resistance of the cell is reduced by CNT addition.

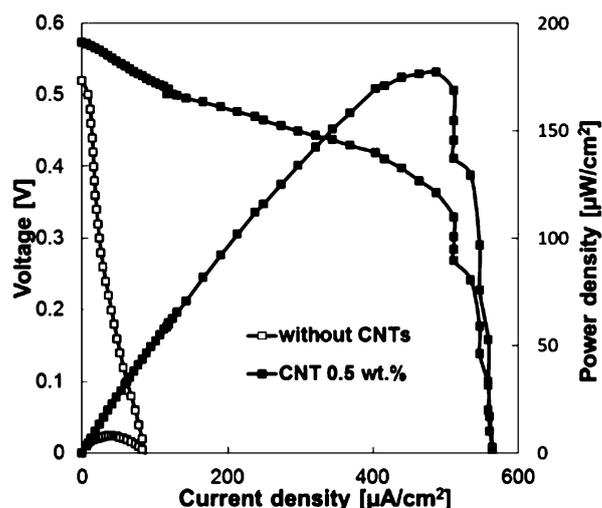


FIG. 7. Current-voltage and current-power curves in cases with and without synthesized CNTs.

In summary, we proposed a three-dimensional conductive network of dispersed CNTs for microbial fuel cells and synthesized CNTs suited to our purpose by a thermal CVD method. By dispersing the synthesized CNTs in an anode solution at a concentration of 0.5 wt.%, we realized a markedly increased power density of $176 \mu\text{W}/\text{cm}^2$, which is approximately 29-fold higher than that in the case without CNTs. These results led us to the conclusion that the three-dimensional CNT network has a significant contribution in the partial use of MFCs.

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