

Development of platinum supported on single-walled carbon nanotubes by deposition-precipitation for microbial fuel cells

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ABSTRACT

Microbial fuel cells (MFCs) are an ecologically friendly technology that can recover electricity and simultaneously treat wastewater. Among all the influential factors, cathode material and catalyst play a crucial role in electricity production and oxygen reduction. In this study, Pt nanocatalysts deposited on single-walled carbon nanotubes (Pt/SWCNTs) were synthesized by the deposition-precipitation (DP) method under optimal conditions. The results show that DP might be a promising method for the preparation of Pt/SWCNTs due to its simple, cost-effective and time-saving procedure, in addition to being highly efficient at creating small Pt particles (0.9 nm) that were very uniformly distributed. The synthesized Pt/SWCNTs suspension was spray-coated on to carbon cloth and then used as a cathode for MFCs. The electricity generation of MFCs equipped with a Pt/SWCNTs cathode was evaluated in terms of open circuit voltage (0.6954 V), internal resistance ($63.3 \Omega \cdot m^2$) and maximum power density ($2,022 \text{ mW}/m^2$). The chemical oxygen demand removal, biological oxygen demand removal, total dissolved solids removal, total suspended solids removal and silver recovery was satisfactory at 84.5%, 74.0%, 45.7%, 60.0% and 99.0%, respectively. Therefore, Pt/SWCNTs from the DP method was identified as a potential candidate to replace commercial Pt-carbon cloth for MFC cathodes.

Key words | cathode, deposition-precipitation, microbial fuel cell, platinum, single-walled carbon nanotubes

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INTRODUCTION

Microbial fuel cells (MFCs) are an ecologically friendly method that can treat wastewater and simultaneously recover electrical energy directly from a variety of organic matter. MFCs use bacteria in wastewater as catalysts to directly convert organic matter to carbon dioxide, water and energy (Logan *et al.* 2006). Another potential application of MFCs is to remove and recover metals from wastewater. At the cathode, the metal is reduced to its metallic form and deposited on the cathode surface. At the anode, electrical energy can be obtained from the oxidation of organic matter (Ter Heijne *et al.* 2010; Tao *et al.* 2012).

Among the factors that influence MFC performance, both cathode and catalyst play integral roles in electricity generation, organic removal efficiency and metal removal efficiency. At the cathode, oxygen is the most suitable electron acceptor. However, the oxygen reduction reaction (ORR) is slow, leading to high reduction overpotential.

Therefore, a catalyst is generally required to decrease the activation energy of ORR (Rismani-Yazdi *et al.* 2008). It is known that a catalyst support affects the stability and performance of the catalyst due to the interaction between the catalyst and support (Shen *et al.* 2008). The specific requirements for catalyst supports include high specific surface area, high conductivity, corrosion resistance and the capability to create anchoring sites with the catalyst (Timur *et al.* 2007). At present, carbon nanotubes (CNTs) are attractive candidates as both catalyst support and cathode material due to their excellent structural, physical and chemical properties (Qiao *et al.* 2007; Timur *et al.* 2007).

Platinum (Pt) is currently the most popular metal catalyst for ORR in MFCs due to its excellent catalytic ability. However, the commercial feasibility of Pt is limited because of its high cost and possible toxicity (He & Angenent 2006). Therefore, the Pt load could be reduced or alternative

catalysts might be investigated. To reduce the Pt load while still maintaining high catalytic ability, a suitable catalyst loading method and a catalyst support with a high specific surface area are the important factors. Various decoration methods of Pt catalysts have been reported for a variety of supporting materials. However, little research has been conducted on CNT supports.

An extensive review of studies conducted on the preparation of Pt decorated CNTs as the cathode material for MFCs is summarized in Table 1. The decoration methods include chemical reduction (Yang *et al.* 2011; Ghasemi *et al.* 2013; Halakoo *et al.* 2015) and electrodeposition (Xie *et al.* 2011; Yen *et al.* 2013; Quan *et al.* 2015). However, the electrodeposition method requires specific and expensive equipment. Also, the chemical reduction method from some studies provided large Pt catalysts with low uniformity on the supports. Alternatively, the deposition-precipitation (DP) method is characterized by the precipitation of the active phase precursor on the surface of the supports, followed by crystallographic deposition. Typically, DP is a simple, cost-effective, time-saving and efficient decoration method for Au on SiO₂ or TiO₂ supports (Phonthammachai *et al.* 2008; Sandoval *et al.* 2011; Ruiz *et al.* 2013), but it has scarcely been used to prepare supported Pt catalysts. To date, no known research studies on DP for Pt on CNT supports have been reported. Therefore, the decoration of Pt catalysts on CNT supports by DP needs to be further investigated in order to obtain small particles of Pt catalyst that are very uniformly dispersed, resulting in improvement of catalytic ability.

In this study, Pt nanocatalysts supported on single-walled CNTs (Pt/SWCNTs) were synthesized by DP. The properties of synthesized Pt/SWCNTs were evaluated based on morphology, composition and size distribution. The Pt/SWCNTs were sprayed onto carbon cloth and used as a cathode. The performance of MFCs equipped with Pt/SWCNTs spray-coated onto carbon cloth was evaluated in

terms of electricity generation, organic removal efficiency and metal recovery. In addition, the performance of these MFCs, using Pt/SWCNTs spray-coated onto carbon cloth as cathodes, was compared with SWCNTs spray-coated onto carbon cloth, commercial Pt-carbon cloth and plain carbon cloth. In addition, PTFE membrane replaced Nafion membrane and used as the electrolyte for reasons of cost.

MATERIALS AND METHODS

Preparation of Pt/SWCNTs-COOH

Pt catalysts on SWCNTs-COOH were prepared by DP. Single-walled CNTs with carboxyl functional groups (SWCNTs-COOH; Carbon Solutions Inc., USA) were ultrasonically dispersed in deionized water for 60 min. The SWCNTs-COOH suspension was mixed with 1.5 mM chloroplatinic acid hexahydrate solution (H₂PtCl₆·6H₂O; Sigma-Aldrich, USA), followed by adjustment of pH to 7. The suspension was then vigorously stirred at a reaction temperature of 80 °C for 60 min to produce the Pt/SWCNTs-COOH.

Cathode preparation

The synthesized Pt/SWCNTs-COOH and SWCNTs-COOH were coated onto a carbon cloth (non-wet-proofed, type B, E-TEK, USA). For this purpose, 1% (v/v) Nafion 117 (Sigma-Aldrich, USA) was added to the CNTs suspension and ultrasonically dispersed for 60 min. Then, the suspension was spray-coated onto carbon cloth at a Pt loading of 0.2 mg/cm² by air-brush and dried on a hotplate. In addition, carbon cloth (non-wet proofed, type B, E-TEK, USA) and commercial Pt-carbon cloth (0.2 mg/cm², Fuel Cells Etc, USA) were used for comparison with SWCNTs-COOH-based cathode.

Table 1 | Literature review of MFCs equipped with Pt/CNT-based cathodes from various decoration methods

Cathode material	Supporting material	Catalyst	Decoration method	P _{max} (mW/m ²)	References
Carbon paper	CNTs	Pt	Chemical reduction	147	Halakoo <i>et al.</i> (2015)
Carbon paper	MWCNTs	Pt-Pd	Electrodeposition	762	Quan <i>et al.</i> (2015)
Carbon paper	CNTs	Pt	Chemical reduction	169	Ghasemi <i>et al.</i> (2013)
Carbon cloth	MWCNTs	Pt	Electrodeposition	59	Yen <i>et al.</i> (2013)
Carbon paper	Polyamidoamine-DENs	Pt	Chemical reduction	630	Yang <i>et al.</i> (2011)
Textile	SWCNTs	Pt	Electrodeposition	837	Xie <i>et al.</i> (2011)
Carbon cloth	SWCNTs-COOH	Pt	Deposition-precipitation		In this work

Cathode characterization

The morphology and size distribution of the synthesized Pt/SWCNTs-COOH were characterized by a transmission electron microscope (TEM, JEOL, JEM-2100, Japan) operating at 200 kV. The samples were prepared by placing a drop of suspension onto a formvar carbon-coated copper grid (FCF300-Cu, Electron Microscopy Sciences, USA) and dried at room temperature.

The crystalline structures of the synthesized Pt/SWCNTs-COOH were measured with an X-ray powder diffractometer (XRD, XRD-6000, Shimadzu, Japan). Cu K α -ray operating at 40 kv and 30 mA was used as the X-ray source. The reflections in powder XRD were obtained in the 2θ range between 10–85°.

The structure and composition of the cathodes were determined by a field emission scanning electron microscope-energy dispersive X-ray spectroscopy (FESEM-EDX, JEOL, JSM7610F, Japan). The samples were mounted onto an aluminum stub prior to measurement.

MFC construction and operation

H-shaped dual-chamber MFC reactors, each with an electrode chamber holding a volume of 600 mL were constructed. The chambers were separated with polytetrafluoroethylene (PTFE) membrane (0.45- μ m pore-sized, Sartorius Stedim Biotech, Germany). In this study, the PTFE membrane replaced Nafion membrane, which is generally used as proton exchange membrane (PEM). From an economic point of view, PTFE membrane was found to be a cost-effective (US\$4.03/reactor), which was 4.41 times lower than Nafion (US\$17.79/reactor). The apparent anode and cathode surface areas were similar at 25 cm² each. Nichrome wires were used to connect each electrode to the external circuit. Four different types of MFC reactors were constructed (Table 2).

Canteen wastewater collected from the septic tank of the Srakaew canteen at Silpakorn University, Thailand, was used as the inoculum and substrate. The canteen wastewater

had a chemical oxygen demand (COD) ranging from 720–1,200 mg O₂/L, biological oxygen demand (BOD) ranging from 290–390 mg O₂/L, total dissolved solids (TDS) ranging from 1,200–1,600 mg/L and total suspended solids (TSS) ranging from 50–120 mg/L. The cathode chamber was filled with a mixture of NaCl and NaHCO₃ and aerated to provide O₂ as the electron acceptor. For the metal recovery study, 100 ppm of AgNO₃ solution (Chemisches Laboratorium, Germany) was placed in the cathode chamber and used as the electron acceptor. N₂ gas was used to purge the chamber for 15 min. All the reactors were operated in batch reactor mode at room temperature (30 \pm 2 °C).

Analysis of MFC performances

The MFC reactors were evaluated including electricity production, organic removal efficiency and metal recovery. The voltage (*V*) of the MFC was continuously measured every 30 min by a data logger with a computerized data acquisition system (GL220, Graphtec, Japan). The power density (*P*, mW/m²) was calculated from $P = IV/A$, where *I* is the current, *V* is the voltage and *A* is the surface area of cathode. Polarization curves were drawn by changing the external resistance from 900,000 to 10 Ω and then used to determine the open circuit voltage (OCV), the internal resistance (*R*_{int}) and the maximum power density (*P*_{max}) (Logan et al. 2006).

The COD and BOD concentrations of the influents and effluents were measured according to the American Public Health Association's *Standard Methods* (APHA 2012) to calculate %COD removal and %BOD removal. TDS and TSS concentrations of the influents and effluents were measured by gravimetric analysis according to the American Society for Testing and Materials' *Standard Test Methods* (ASTM 2013) to calculate %TDS removal and %TSS removal. The silver ion concentrations before and after operation of MFCs were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent, 710, USA) at 328.068 nm to calculate silver recovery.

RESULTS AND DISCUSSION

Catalyst characterization

Morphology and size distribution of catalyst

As shown in Figure 1(a), the SWCNTs-COOH dispersed in deionized water (DI) water presented a well-defined tube

Table 2 | Detailed list of electrodes for each MFC set-up

	Anode	Cathode
MFC-1	Carbon cloth	Carbon cloth
MFC-2	Carbon cloth	SWCNTs-COOH on carbon cloth
MFC-3	Carbon cloth	Pt/SWCNTs-COOH on carbon cloth
MFC-4	Carbon cloth	Commercial Pt-carbon cloth

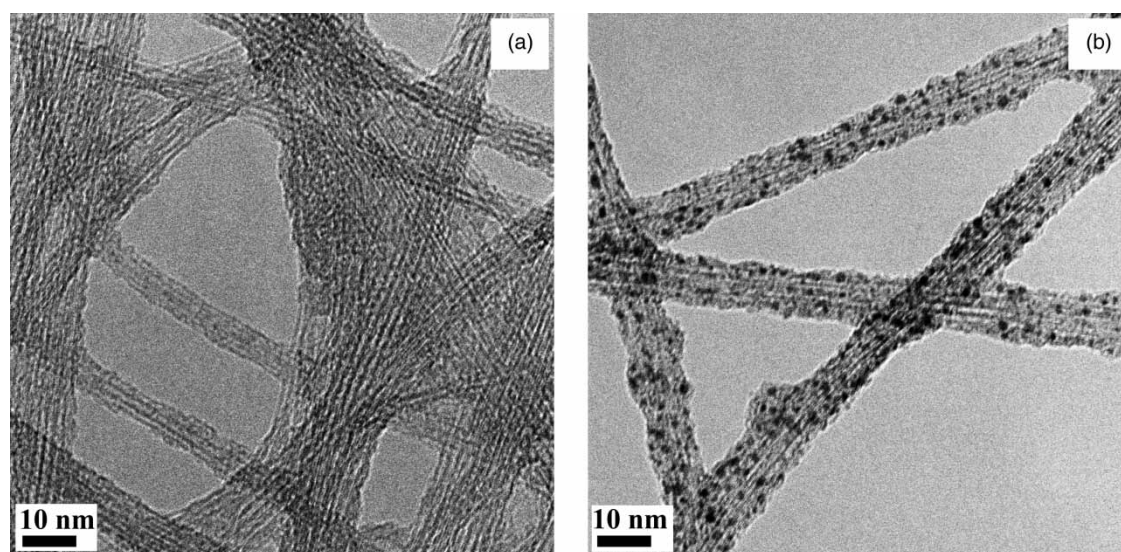


Figure 1 | TEM images of CNTs dispersed in DI water: (a) SWCNTs-COOH; and (b) Pt/SWCNTs-COOH.

structure with outer diameter ranging from 5 to 15 nm. In order to improve catalytic ability, Pt nanocatalysts were prepared by the DP method. The spherical-shaped Pt nanocatalysts on the SWCNT surfaces are shown in [Figure 1\(b\)](#). At optimal DP conditions, Pt nanocatalysts are small in size and uniformly distributed on the SWCNTs-COOH. The particle size of Pt nanocatalysts was in the range of 0.4 to 1.6 nm and demonstrated the highest distribution at 0.9 nm. It is worth noting that this was the first study which demonstrates the achievement of small and highly active Pt nanocatalysts on SWCNTs-COOH using the simple, cost-effective and time-saving DP method. In addition, the average size of Pt nanocatalysts (0.9 nm) in this study was competitive when compared to those from chemical reduction ([Yang *et al.* 2011](#); [Ghasemi *et al.* 2013](#); [Halakoo *et al.* 2015](#)) and electrodeposition ([Xie *et al.* 2011](#); [Yen *et al.* 2013](#); [Quan *et al.* 2015](#)).

Structure and composition of catalyst

The XRD patterns of SWCNTs-COOH and Pt/SWCNTs-COOH are illustrated in [Figure 2](#). The peaks at $2\theta = 26.48^\circ$, 44.56° and 51.95° could be attributed to the diffractions of the (002), (100) and (004) planes of the hexagonal structure of graphite. Those appearing at $2\theta = 38.46^\circ$, 44.72° , 65.06° , 78.18° and 82.42° indicated five characteristic Pt reflections corresponding to the (111), (200), (220), (311) and (222) planes. As such, they showed that Pt nanocatalysts were deposited on SWCNT surfaces and the crystallite planes correspond to the face-centered cubic lattice structure of the Pt nanocatalysts. Similar XRD patterns of Pt and SWCNTs-

COOH have been reported in the literature ([Niu & Wang 2008](#); [Hsieh & Lin 2009](#); [Basu & Basu 2011](#)).

The FESEM-EDX ([Figure 3](#)) spectrums show the presence of SWCNTs and Pt respectively, indicating the successful deposition of Pt nanocatalysts on SWCNTs. In addition, the high intensity peaks substantiated the high loading.

Cathode characterization

The surface morphological images of all types of cathodes, as observed by FESEM, are shown in [Figure 4](#). The smooth and straight fibres from plain carbon cloth are shown in [Figure 4\(a\)](#). Both CNT-based cathodes clearly show a uniform distribution of highly entangled three-dimensional CNT networks ([Figure 4\(c\)](#) and [4\(d\)](#)) which might assist the deposition of nanocatalyst and serve as nanowires to support electron transfer ([Wang *et al.* 2011](#); [Zhang *et al.* 2011](#)). This structure might improve the transition catalytic ability due to its impact on the three-phase ORR ([Lefebvre *et al.* 2012](#)). In addition, the results from EDX element mappings ([Figure 5](#)) indicated that Pt from Pt/SWCNTs-COOH provided a higher distribution than that from commercial Pt-carbon cloth.

MFC performance

Electrical performance of MFCs

The average electrical performance of MFCs equipped with a variety of cathodes is summarized in [Table 3](#). In

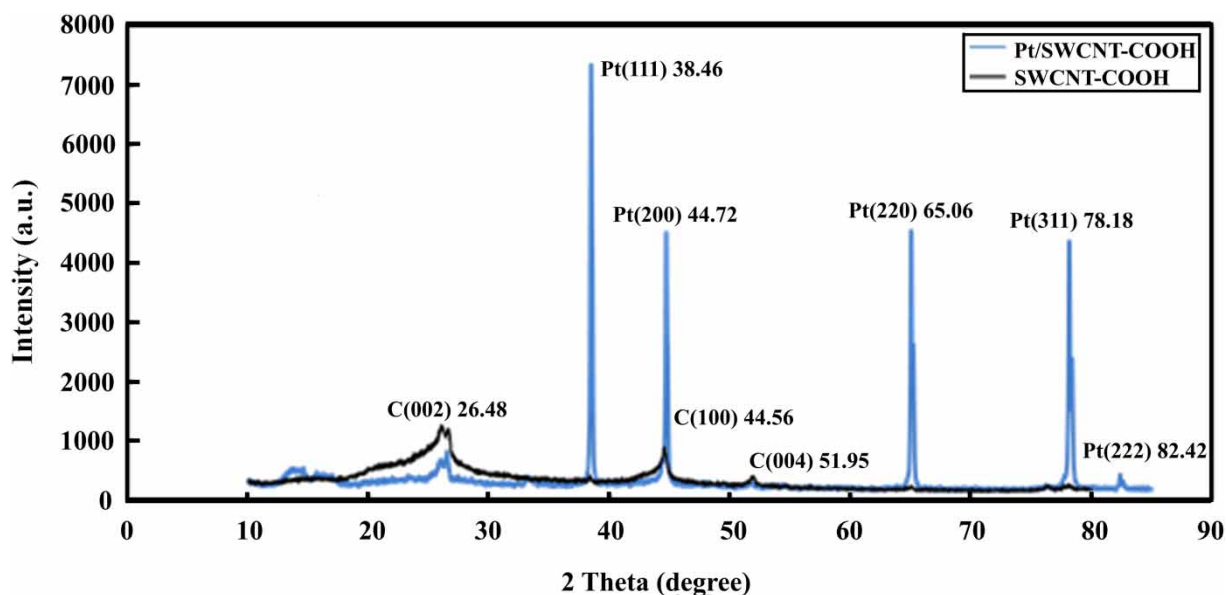


Figure 2 | XRD spectrums of SWCNTs-COOH and Pt/SWCNTs-COOH.

comparison to cathodes without a catalyst, cathodes with Pt catalysts displayed high electrical performance. This excellent performance could be directly related to the catalyst deposited on supporting materials which decreased the activation energy barrier and improved the kinetics of ORR at the cathode surfaces (Rismani-Yazdi *et al.* 2008). Among MFCs equipped with a non-catalyst cathode, the MFC with SWCNTs-COOH/carbon cloth exhibited higher OCV and P_{\max} (0.5022 V and 1,698 mW/m^2) than the MFC with carbon cloth (0.4657 V and 1,632 mW/m^2) (Figure 6). This could be due to the excellent conductivity, high specific surface area and three-dimensional network structure of SWCNTs-COOH, which enhanced active spaces for ORR and improved electron transfer capability (Wang *et al.* 2011; Thepsuparungsikul *et al.* 2014). MFCs equipped

with cathodes coated with Pt catalysts displayed high OCV and high P_{\max} , which is in the highest tier in MFC research. The P_{\max} values obtained from Pt/SWCNTs-COOH/carbon cloth (2,022 mW/m^2) and commercial Pt-carbon cloth (3,055 mW/m^2) were higher than those reported in literature (Table 1). Comparable results of OCV were obtained at $p > 0.05$ by analysis of variance (ANOVA) indicating no significant differences among cathode materials with Pt catalyst. In addition, the %RSD obtained from MFCs with different cathode materials was less than 5% ($n = 3$), demonstrating high precision in terms of MFC electrical performance. In conclusion, high catalytic ability from small and uniform dispersion of Pt nanocatalysts from DP together with excellent properties of SWCNTs-COOH resulted in improvement

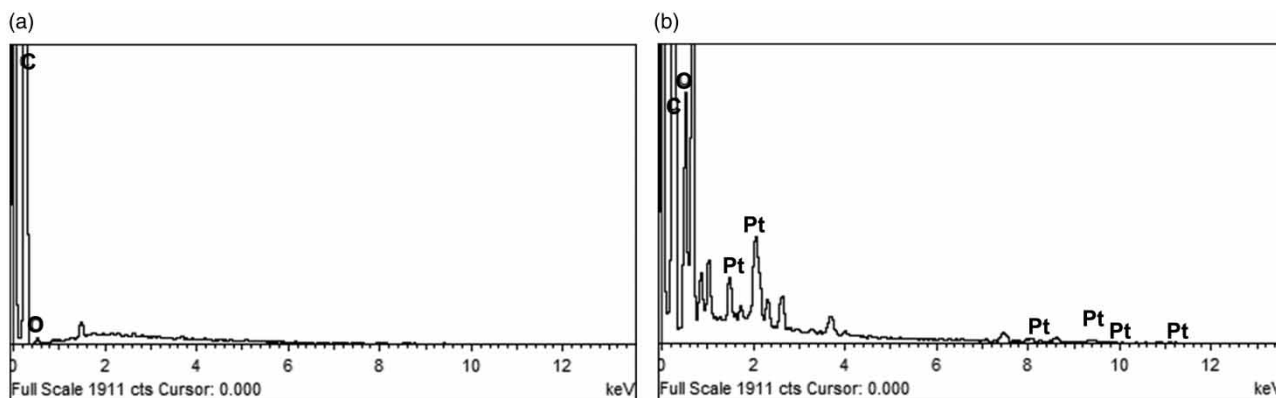


Figure 3 | FESEM-EDX spectrums: (a) SWCNTs-COOH; and (b) Pt/SWCNTs-COOH.

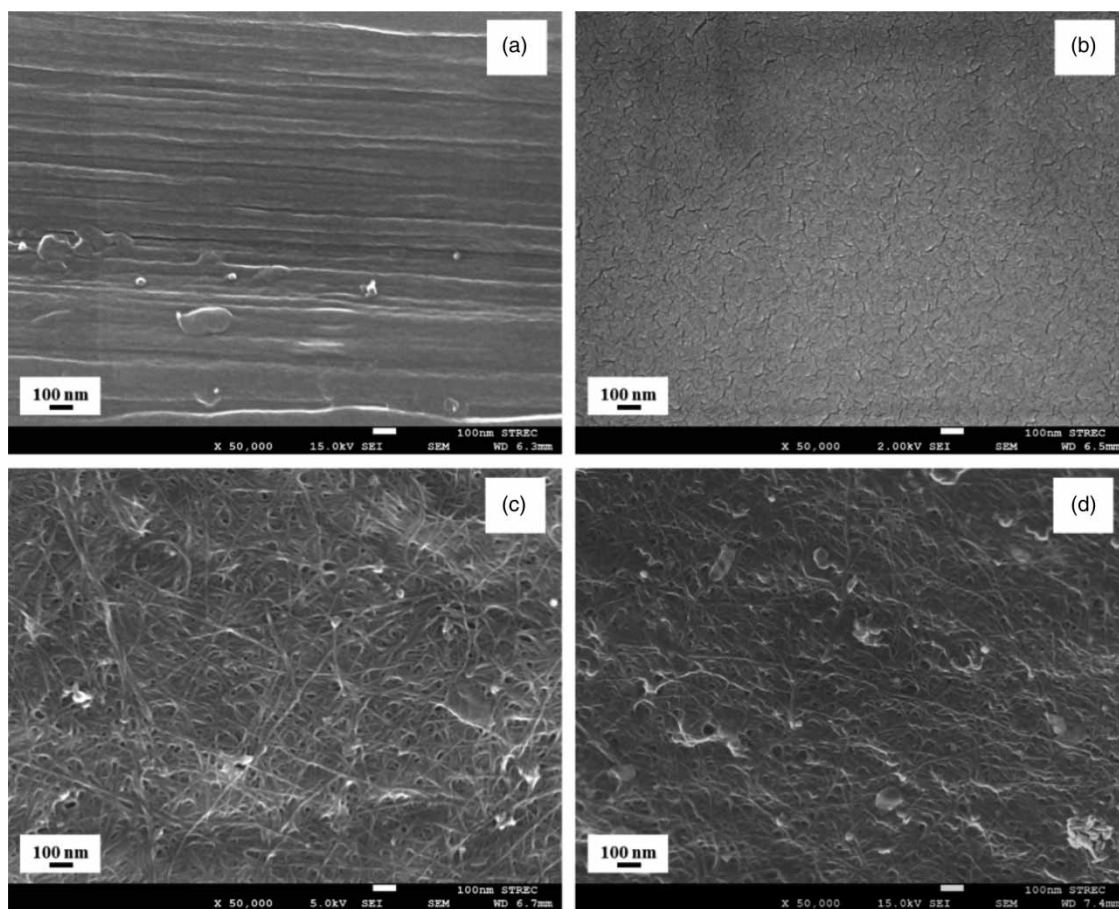


Figure 4 | FESEM images of cathodes (50,000x magnification): (a) carbon cloth; (b) commercial Pt-carbon cloth; (c) SWCNTs-COOH on carbon cloth; and (d) Pt/SWCNTs-COOH on carbon cloth.

of MFC performance. From an economic point of view, Pt/SWCNTs-COOH/carbon cloth proved cost-effective, being 15% lower in cost compared to commercial Pt-

carbon cloth. Therefore, Pt/SWCNTs from DP was identified as a potential candidate to replace commercial Pt-carbon cloth for MFC cathodes.

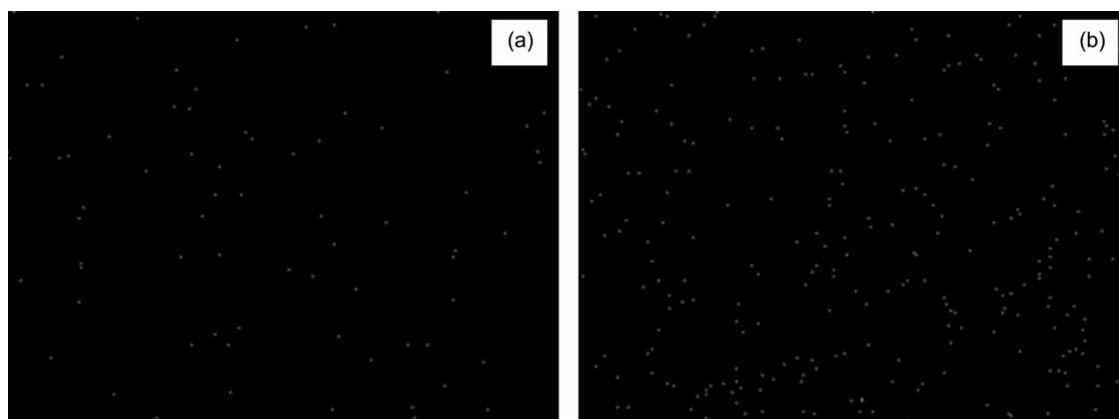
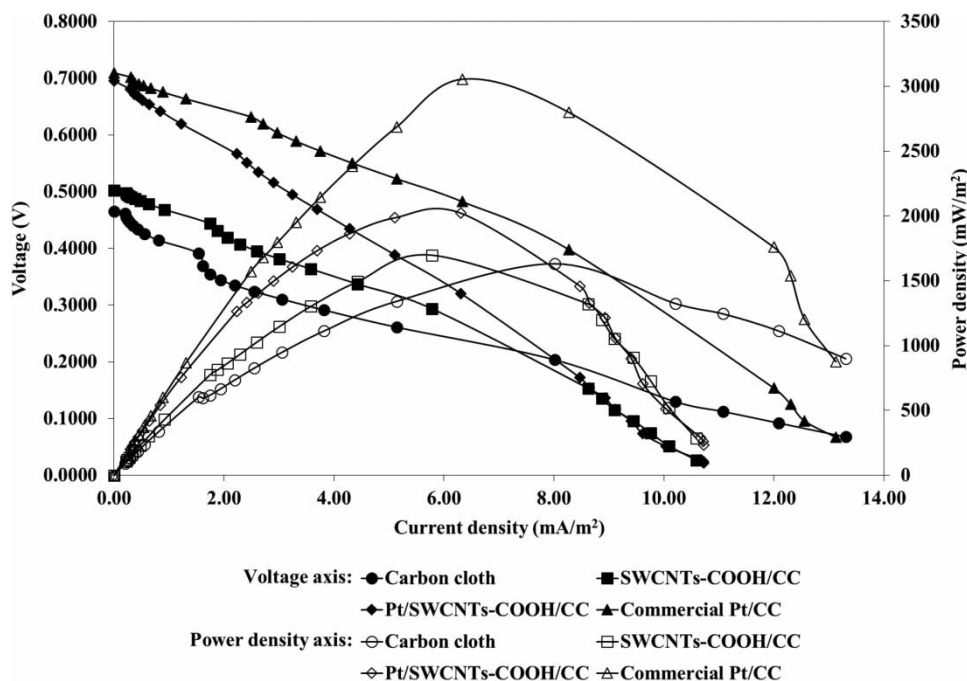


Figure 5 | EDX element mappings of Pt from cathodes: (a) commercial Pt-carbon cloth; and (b) Pt/SWCNTs-COOH on carbon cloth.

Table 3 | MFC electrical performance using various cathodes

MFC	OCV (V)	Internal resistance ($\Omega \cdot m^2$)	Maximum power density (mW/m^2)
Carbon cloth	0.4657 ± 0.0084	29.4 ± 1.0	$1,632 \pm 23$
SWCNTs-COOH on carbon cloth	0.5022 ± 0.0097	43.5 ± 2.2	$1,698 \pm 27$
Pt/SWCNTs-COOH on carbon cloth	0.6954 ± 0.0071	63.3 ± 2.6	$2,022 \pm 24$
Commercial Pt-carbon cloth	0.7095 ± 0.0074	47.6 ± 1.4	$3,055 \pm 44$

**Figure 6** | (a) Polarization curves and (b) power density curves obtained with MFCs equipped with different types of cathodes.

Organic removal efficiency and metal recovery of MFCs

The COD, BOD, TDS and TSS removal efficiencies are summarized in Table 4. From MFCs with all types of cathodes, COD removal efficiencies were over 80%, while BOD removal efficiencies ranged from 69.3 to 74.5%. TDS and TSS removal efficiencies ranged from 43.7 to 46.4% and from 57.1 to 68.5%, respectively. From Table 4, the %RSD of all MFCs was less than 10% ($n=3$), demonstrating

good precision in terms of organic removal efficiencies. Results showed that no significant differences at a 95% confidence level in organic removal efficiencies were observed regardless of the presence of Pt and types of supporting materials used at the cathode. In addition, the organic removal efficiencies of SWCNT-based cathode MFCs in this study were competitive when compared to the published literature with commercial Pt-carbon cloth cathodes (Lorenzo *et al.* 2010) and with CNT-based cathodes (Tsai

Table 4 | Organic removal efficiencies and % Ag recovery achieved by MFCs using various cathodes

MFC	COD removal (%)	BOD removal (%)	TDS removal (%)	TSS removal (%)	% Ag recovery
Carbon cloth	85.9 ± 2.9	69.3 ± 3.9	43.9 ± 2.6	57.1 ± 2.2	46.0 ± 3.5
SWCNTs-COOH on carbon cloth	84.9 ± 3.6	74.5 ± 4.5	43.7 ± 3.9	68.5 ± 3.4	49.4 ± 3.9
Pt/SWCNTs-COOH on carbon cloth	84.5 ± 3.2	74.0 ± 4.2	45.7 ± 3.5	60.0 ± 3.5	99.0 ± 2.8
Commercial Pt-carbon cloth	82.9 ± 3.0	71.0 ± 4.3	46.4 ± 4.7	58.4 ± 4.2	74.1 ± 3.0

et al. 2009; Lu et al. 2011). For the silver recovery study, the shiny rods of silver on the cathode surfaces were visibly observed in all MFCs. The MFC equipped with Pt/SWCNTs-COOH on the carbon-cloth cathode achieved the highest silver recovery of 99% and showed a significant difference ($p < 0.0001$) to other cathode materials. Overall, all results indicated the potential of MFCs to recover and remove silver from wastewater.

CONCLUSION

Pt/SWCNTs-COOH coated onto carbon cloth was identified as a potential material to replace commercial Pt-carbon cloth for MFC cathodes. Pt/SWCNTs-based cathodes from the DP method displayed an improvement of MFC performance and reduction of cathode cost due to small particles of Pt that are very uniformly distributed, together with supporting material from SWCNTs. Moreover, the DP method was a simple, cost-effective and time-saving procedure. Pt/SWCNTs-COOH/carbon cloth as a cathode and carbon cloth as an anode greatly increased the OCV (0.6954 V) of the MFC system and generated P_{\max} 1.2-fold higher than plain carbon cloth. In addition, the COD removal efficiency and silver recovery were very satisfactory at 84.5% and 99.0%, respectively.

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REFERENCES

- APHA 2012 *Standard Methods for the Examination of Water and Wastewater* (E. Rice, R. Baird, A. Eaton & L. Clesceri, eds), 22nd edn. American Public Health Association/American Water Works Association, Water Environmental Federation, Washington, DC, USA.
- ASTM 2013 *Standard Test Methods for Filterable Matter (Total Dissolved Solids) and Nonfilterable Matter (Total Suspended Solids) in Water: D13-5907*. American Society for Testing and Materials Annual Book of ASTM Standards, Pennsylvania, USA.
- Basu, D. & Basu, S. 2011 Performance studies of Pd-Pt and Pt-Pd-Au catalysts for electro-oxidation of glucose in direct glucose fuel cell. *Int. J. Hydrogen Energy* **36**, 14923–14929.
- Ghasemi, M., Ismail, M., Kamarudin, S. K., Saeedfar, K., Daud, W. R. W., Hassan, S. H. A., Heng, L. Y., Alam, J. & Oh, S. E. 2013 Carbon nanotube as an alternative cathode support and catalyst for microbial fuel cells. *Appl. Energy* **102**, 1050–1056.
- Halakoo, E., Khademi, A., Ghasemi, M., Yusof, M. N., Gohari, R. J. & Ismail, A. F. 2015 Production of sustainable energy by carbon nanotube/platinum catalyst in microbial fuel cell. *Procedia CIRP* **26**, 473–476.
- He, Z. & Angenent, L. 2006 Application of bacterial biocathodes in microbial fuel cells. *Electroanalysis* **18**, 2009–2015.
- Hsieh, C.-T. & Lin, J. Y. 2009 Fabrication of bimetallic Pt-M (M = Fe, Co, and Ni) nanoparticle/carbon nanotube electrocatalysts for direct methanol fuel cells. *J. Power Sources* **188**, 347–352.
- Lefebvre, O., Tang, Z., Fung, M. P. H., Chua, D. H. C., Chang, I. S. & Ng, H. Y. 2012 Electrical performance of low cost cathodes prepared by plasma sputtering deposition in microbial fuel cells. *Biosens. Bioelectron.* **31**, 164–169.
- Logan, B. E., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. & Rabaey, K. 2006 Microbial fuel cells: methodology and technology. *Environ. Sci. Technol.* **40**, 5181–5192.
- Lorenzo, M. D., Scott, K., Curtis, T. P. & Head, I. M. 2010 Effect of increasing anode surface area on the performance of a single chamber microbial fuel cell. *Chem. Eng. J.* **156**, 40–48.
- Lu, M., Kharkwal, S., Ng, H. Y. & Li, S. F. Y. 2011 Carbon nanotube supported mno_2 catalysts for oxygen reduction reaction and their applications in microbial fuel cell. *Biosens. Bioelectron.* **26**, 4728–4732.
- Niu, J. J. & Wang, J. W. 2008 Activated carbon nanotubes-supported catalyst in fuel cells. *Electrochim. Acta* **53**, 8058–8063.
- Phonthammachai, N., Kah, J. C. Y., Jun, G., Sheppard, C. J. R., Olivo, M. C., Mhaisalkar, S. G. & White, T. J. 2008 Synthesis of contiguous silica-gold core-shell structures: critical parameters and processes. *Langmuir* **24**, 5109–5112.
- Qiao, Y., Li, C. M., Bao, S.-J. & Bao, Q.-L. 2007 Carbon nanotube/polyaniline composite as anode material for microbial fuel cells. *J. Power Sources* **170**, 79–84.
- Quan, X., Mei, Y., Xu, H., Sun, B. & Zhang, X. 2015 Optimization of Pt-Pd alloy catalyst and supporting materials for oxygen reduction in air-cathode microbial fuel cells. *Electrochim. Acta* **165**, 72–77.
- Rismani-Yazdi, H., Carver, S. M., Christy, A. D. & Tuovinen, O. H. 2008 Cathodic limitations in microbial fuel cells: an overview. *J. Power Sources* **180**, 683–694.
- Ruiz, S. O., Zanella, R., López, R., Gordillo, A. H. & Gómez, R. 2013 Photocatalyst hydrogen production by water/methanol decomposition using Au/TiO₂ prepared by deposition-precipitation with urea. *J. Hazard. Mater.* **263P**, 2–10.
- Sandoval, A., Aguilar, A., Louis, C., Traverse, A. & Zanella, R. 2011 Bimetallic Au-Ag/TiO₂ catalyst prepared by deposition-precipitation: high activity and stability in CO oxidation. *J. Catal.* **281**, 40–49.

- Shen, J., Hu, Y., Li, C., Qin, C. & Ye, M. 2008 Pt-Co supported on single-walled carbon nanotubes as an anode catalyst for direct methanol fuel cells. *Electrochim. Acta* **53**, 7276–7280.
- Tao, H.-C., Gao, Z.-Y., Ding, H., Nan, X. & Wu, W.-M. 2012 Recovery of silver from silver (I)-containing solutions in bioelectrochemical reactors. *Bioresour. Technol.* **111**, 92–97.
- Ter Heijne, A., Liu, F., van der Weijden, R., Weijma, J., Buisman, C. J. N. & Hamelers, H. V. M. 2010 Copper recovery combined with electricity production in a microbial fuel cell. *Environ. Sci. Technol.* **44**, 4376–4381.
- Thepsarungsikul, N., Ng, T. C., Lefebvre, O. & Ng, H. Y. 2014 Different types of carbon nanotube-based anodes to improve microbial fuel cell performance. *Water Sci. Technol.* **69**, 1900–1910.
- Timur, S., Anik, U., Odaci, D. & Gorton, L. 2007 Development of a microbial biosensor based on carbon nanotube (CNT) modified electrodes. *Electrochem. Commun.* **9**, 1810–1815.
- Tsai, H.-Y., Wu, C.-C., Lee, C.-Y. & Shih, E. P. 2009 Microbial fuel cell performance of multiwall carbon nanotubes on carbon cloth as electrodes. *J. Power Sources* **194**, 199–205.
- Wang, H., Wu, Z., Plaseied, A., Jenkins, P., Simpson, L., Engrakul, C. & Ren, Z. 2011 Carbon nanotubes modified air-cathodes for electricity production in microbial fuel cells. *J. Power Sources* **196**, 7465–7469.
- Xie, X., Pasta, M., Hu, L., Yang, Y., McDonough, J., Cha, J., Criddle, C. S. & Cui, Y. 2011 Nano-structured textiles as high-performance aqueous cathodes for microbial fuel cells. *Energy Environ. Sci.* **4**, 1293–1297.
- Yang, X., Lu, J., Zhu, Y., Shen, J., Zhang, Z., Zhang, J., Chen, C. & Li, C. 2011 Microbial fuel cell cathode with dendrimer encapsulated Pt nanoparticles as catalyst. *J. Power Sources* **196**, 10611–10615.
- Yen, S. J., Tsai, M. C., Wang, Z. C., Peng, H. L., Tsai, C. H. & Yew, T. R. 2013 The improvement of catalytic efficiency by optimizing Pt on carbon cloth as a cathode of a microbial fuel cell. *Electrochim. Acta* **108**, 241–247.
- Zhang, Y., Hu, Y., Li, S., Sun, J. & Hou, B. 2011 Manganese dioxide-coated carbon nanotubes as an improved cathodic catalyst for oxygen reduction in a microbial fuel cell. *J. Power Sources* **196**, 9284–9289.

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