Sewage sludge-derived carbon-doped manganese as efficient cathode catalysts in microbial fuel cells

Jingjing Huang, Huajun Feng, Yufeng Jia, Dongsheng Shen and Yingfeng Xu

ABSTRACT

Searching for efficient and inexpensive catalysts to replace precious metal-based catalyst in air-cathode microbial fuel cells is crucial for the practical application and commercialization in wastewater treatment and energy generation. Here, through a simple pyrolysis process, sewage sludge could be converted into carbon material with hierarchically porous structure, which demonstrates oxygen reduction reaction (ORR) catalytic performance. Subsequently, co-doping Mn and N species on the carbonized sewage sludge matrix could further improve the ORR catalytic performance, which even demonstrates comparable performance to the commercial expensive Pt/C catalyst in air-cathode microbial fuels cells (MFC). The highest maximum power density of MFC with Mn-N/SC air-cathode is as high as 1,120 mW m^{-2}, which is similar to the power density of the air-cathode MFC equipped commercialized Pt/C catalyst (1,240 mW m^{-2}). Considering the simple operation, significant cost-saving and easy scale-up of the proposed 'trash-to-treasure' method, it is promising to convert harmful sewage sludge into efficient non-platinum cathode catalysts in microbial fuel cells.

Key words | air-cathode microbial fuel cells, co-doping, non-platinum catalysts, sewage sludge

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INTRODUCTION

With current rapid industrialization, water pollution has been becoming the leading global threat to human lives (Huang *et al.* 2017). Sewage treatment has been widely used for wastewater purification due to the efficient pollutant removal ability and cost-effectiveness, which, however, could produce large amounts of sewage sludge (SS) during the process (Malińska *et al.* 2016). Usually, the generated SS is treated by landfill, incineration and composting (Jiang *et al.* 2011; Li & Chi 2017; Zhang *et al.* 2017). However, all these methods inevitably cause secondary environmental pollution; for example, the release of a large number of organic pollutants, malodorous gas and pathogens (Johnsson 1994; Sanchez-Monedero *et al.* 2017). Therefore, in view of the sharp increase in the sewage sludge from sewage treatment plants, seeking low-cost, no secondary pollution of sludge treatment is necessary.

As we know, Pt-based materials are often used as a catalyst to facilitate the oxygen reduction reaction (ORR), which is the heart of fuel cell energy conversion processes (Liu & Logan 2004; Logan *et al.* 2007). While due to the scarcity and high cost of Pt, the commercial Pt/C fabricated as cathode materials can account for 40–80% of the microbial fuel cells (MFCs) capital costs (Demirbas *et al.* 2009). Thus, it is important to seek efficient, stable, cost-effective and eco-friendly ORR electrocatalysts for fuel cell cathode construction. Recently, carbon-based materials fabricated from renewable carbonaceous sources, such as coconut shells, wood, lignin (Suhas & Carrott 2007), have demonstrated ORR catalytic activities, which aroused wide research interest as promising alternatives to noble metal for ORR due to their low cost, high thermal/chemical stability and excellent conductivity. For example, Yang *et al.* reported an inexpensive activated carbon (AC) synthesized from bamboo to be used as the ORR catalyst in an air cathode MFC, which could produce a power density of 1,056 mW m^{-2} (Yang *et al.* 2017). Dong *et al.* mixed the AC and polytetrafluoroethylene at a ratio of 6:1 to fabricate the metal-free air cathode, obtaining a current density of 3.4 A m^{-2} (Dong *et al.* 2012). Inspired by the ORR catalytic activities of carbon-based materials and the carbon-rich

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nature of sewage sludge, we propose a 'trash-to-treasure' strategy, in which harmful sewage sludge could be converted into carbon materials with porous structure and abundant surface functional groups, thus the hazardous waste could be positively reutilized as low-cost ORR electrocatalyst.

Furthermore, 3*d* transition metal and non-metal elements are considered as active sites (Jiang *et al.* 2012, 2016; Cao *et al.* 2016; Luo *et al.* 2016), especially Co and Mn-based metal nitrogen/carbon complexes (Li *et al.* 2013a, 2013b; Tang *et al.* 2013). Doping metal and nitrogen atoms into carbon lattices could alter the electronic and geometric structures of carbon, resulting into efficiently enhanced ORR catalytic activities (Volosskiy *et al.* 2016). Accordingly, in this study, a simple and easy scale-up pyrolysis process was designed to convert sewage sludge into carbon materials with hierarchically porous structure. Then, Mn and N species were co-doped on the carbonized sewage sludge matrix (denoted as Mn-N/SC) to enhance its ORR catalytic activity. Based on this well-constructed Mn-N/SC catalyst, its microstructure and chemical property were investigated. Subsequently, the ORR electrocatalytic performance of synthesized Mn-N/SC catalyst in the air cathode MFC was analyzed, which was further compared with commercial Pt/C catalyst. To the best of our knowledge, this is a facile and cost-effective approach to convert the hazardous sewage sludge waste into efficient ORR electrocatalyst, which will be highly promising for environmental and energy applications.

EXPERIMENTAL SECTION

Synthesis of Mn-N/SC catalysts

Briefly, sewage sludge was obtained from the Tianchuang Wastewater Treatment Plant in Hangzhou, China, with a moisture content of 80%. The X-ray photoelectron spectroscopy (XPS) results show that the sludge is mainly composed of carbon and oxygen (Figure S1 in the Supplementary Information). The 40-mesh sieve was used to sieve and filter the sewage sludge to remove large particles, and then dried at 60 °C for 12 hours and then further broken by a grinder (F-P400H, Focucy Co., Ltd, China). The SS was initially carbonized in a tube furnace at 1,200 °C for 120 minutes by raising the temperature at a rate of 15 °C per minute under inert N_2 atmosphere at room pressure to obtain sewage sludge biochar powder. The as-prepared sewage sludge biochar was further ground and passed through a 0.2 mm sieve.

Mn-N/SC catalyst was synthesized according to the following method. 1.4 g $MnCl_2$ and 3.2 g carbamide ($CO(NH_2)_2$) were mixed with 4 g SC powder in deionized water. The pH of the solution was adjusted to 3.5 with 0.01 mmol HCl aqueous solution, and the mixture was kept in a water bath at 85 °C for 12 h. The precipitate was collected, washed with deionized water and ethanol, and then heated in N_2 atmosphere at 800 °C. The as-prepared SC catalyst were treated with the same process without the addition of $MnCl_2$ and $CO(NH_2)_2$).

Fabrication of air-cathode

In our study, two air-cathode MFCs were prepared as parallel controls in order to eliminate contingency. The single-chamber MFC is composed of a cylindrical plexiglass chamber fixed by screws, and its effective volume is 45 mL, as shown in Figure S2. Carbon felt (Longpro Carbon Co. Ltd, USA) with an area of 10 cm^2 was used as the anode in MFC. The air-cathode electrodes were manufactured by the brush method. At first, the obtained Mn-N/SC catalyst was mixed with absolute ethanol by ultrasonication for 15 min to prepare a catalyst ink. Subsequently, the prepared catalyst ink was applied to one side of the previously prepared cathode electrode, which was precoated with a 30% PTFE solution. Finally, the cathode electrode was heated at 320 °C for 20 minutes in a muffle furnace. The loading of Mn-N/SC catalyst is 5 mg cm-2 on the cathode. As a comparison, the dose of Pt/C catalyst (20%, Pt loading, Johnson Matthey, China) was 0.5 mg cm^{-2}.

The reactor is inoculated with (5 mL) fresh anodic effluent of an existing acetate-fed bio-electrochemical reactor that was rich in *Geobacter*. The MFCs were operated at 25 ± 3 °C and fed a 1.0 g/L medium containing acetate, a M9 solution (2 g/L $NaHCO_3$; 4.4 g/L, KH_2PO4; 3.4 g/L, K_2HPO_4; 0.5 g/L NaCl; 0.1 g/L $MgSO_4$; 0.1 g/L NH_4Cl; and 1 mL trace mineral.

Electrochemical measurements

All the electrochemical measurements were made in a three-electrode structure with Ag/AgCl as a reference electrode, and the experiments were repeated and the average was reported in the paper. The prepared air-cathode electrode was used as the work electrode and the commercialized carbon felt (5 cm^2) as the counter electrode. Electrochemical impedance spectroscopy (EIS) of the prepared air-cathode was conducted over the frequency

range of 10,000 Hz – 0.1 Hz at the open circuit potential. Linear sweep voltammetry (LSV) curves were conducted by electrochemical workstation from 0.4 V to −0.4 V with a scan rate of 5 mV s^{-1} in M9 solution under air atmosphere.

Analytical techniques

Scanning electron microscopy (SEM, TESCAN S8000, China) was performed to observe the morphology and structure of the obtained Mn-N/SC catalyst. Brunauer-Emmett-Teller (BET) and total pore volume (Vt) were calculated based on the amount of adsorbed N_2 at a relative pressure P/P0 of 0.99. Raman patterns were recorded with an AvaSpec-ULS2048 instrument (BWTEK, The Netherlands) over the range of 4,000–40 cm^{-1}.

RESULTS AND DISCUSSION

The SS was converted into carbon-based materials through pyrolysis. As shown in SEM images (Figure 1(a) and 1(b)), the carbonized sewage sludge demonstrates micro- and macroporous structures, which helps to provide free internal passage for mass transport to interact with active sites inside (Li *et al.* 2013a, 2013b; Hou *et al.* 2015). Moreover, the micro- and macroporous structures of carbonized sewage sludge could be well-maintained after the co-doping of manganese and nitrogen in carbon materials sewage. Judged from energy-dispersive X-ray (EDX) mapping from different ranges (Figure 1(c) and Figure S3 in the Supplementary Information), Mn and N elements are well-dispersed on the carbon matrix without observable aggregation. The doping amounts of Mn, N are 23.84%, 3.6% respectively,

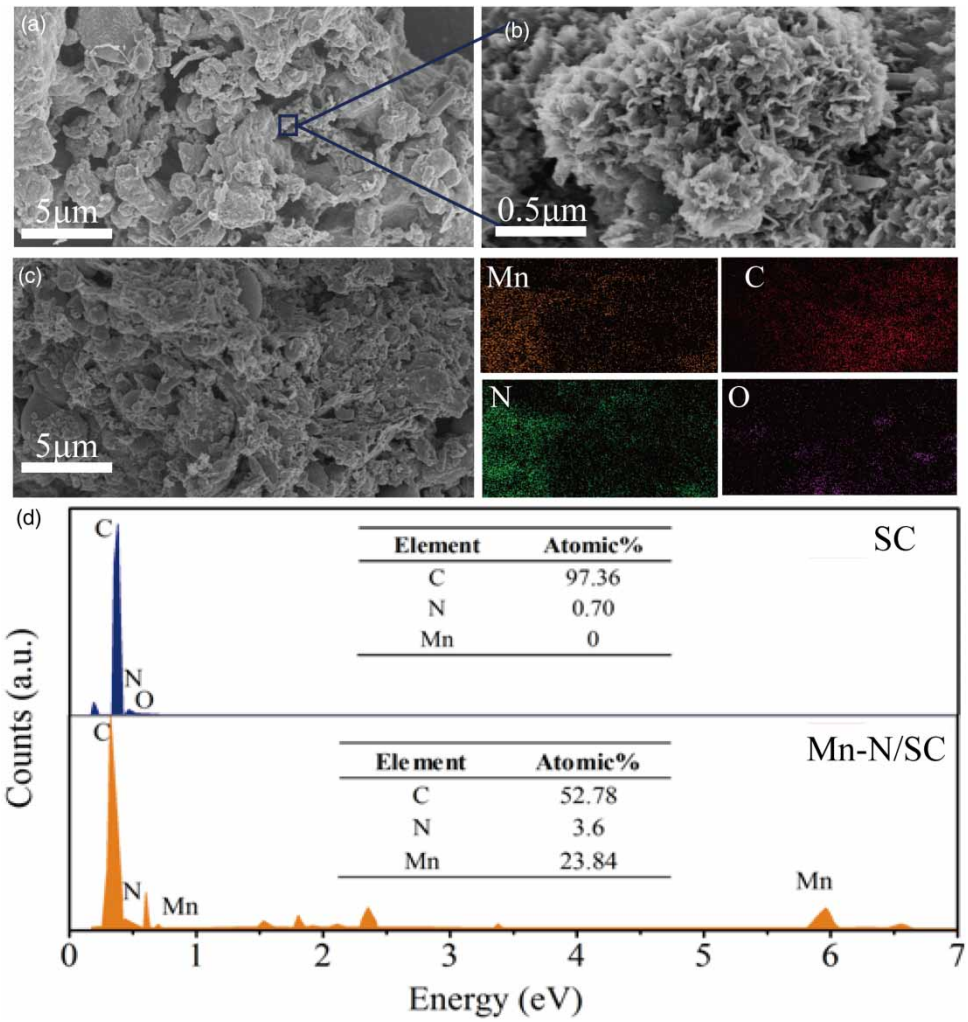

Figure 1 | (a) SEM and (b) high-resolution SEM images of SC, exhibiting the 3D hierarchical porous structure, (c) SEM images of Mn-N/SC and the corresponding element mappings, (d) the corresponding C, N, Mn, O analyses, the insert is the quantitative elemental composition.

is in accordance with XPS results, indicating Mn, N are uniformly doped on the carbonized sewage sludge matrix.

In addition, the N_2 adsorption-desorption isotherms and pore size distributions of the SC and the Mn-N/SC are shown in Figure 2, which confirming the presence of mesoporous structure of the samples, consistent with the SEM results. Compared with SC, Mn-N/SC exhibits higher surface area and pore volume than those of raw SC, which is benefit for the electrochemical performance.

Raman spectra were further conducted to investigate the structure of carbonized sewage sludge (Figure 3(a)). The appearance of two peaks in the Raman spectrum should be ascribed to the D band (1,360 cm^{-1}) and G band (1,570 cm^{-1}) respectively. The G band to the D band intensity ratio (I_G/I_D) is about 1, indicating good graphite structure of SC (Li *et al.* 2013a, 2013b; Xiao *et al.* 2013). Moreover, the I_G/I_D of Mn-N/SC is similar compared with SC, indicating the well-maintained graphite structure of Mn-N/SC after co-doping.

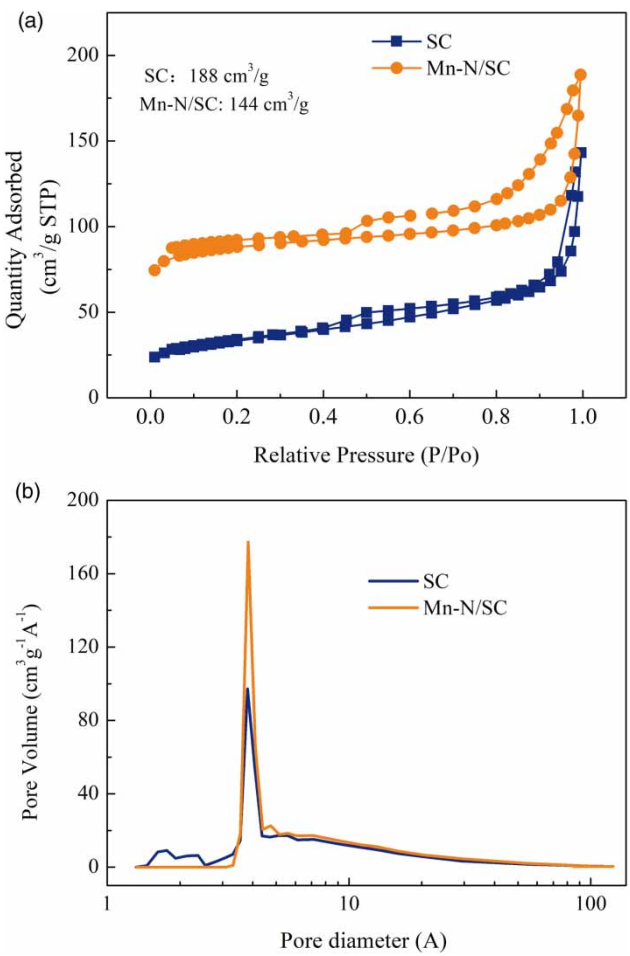

Figure 2 | (a) The N_2 adsorption-desorption isotherms and (b) the pore size distribution of the SC and the Mn-N/SC.

XPS further analysis of the SC and Mn-N/SC samples shows the chemical structures of nitrogen and manganese atoms on the surface of the catalyst (Figure 3(b)–3(d)). The high percentage of C-N bonds indicates the coordination of nitrogen and carbon in Mn-N/SC. Figure 3(c) presents the Mn high-resolution analysis of Mn-N/SC, which contains peaks from Mn $2p_{3/2}$ and Mn $2p_{1/2}$. As shown in Figure 3(d), the N 1 s of Mn-N/SC catalyst can be divided into three individual component peaks, which can be assigned to H-C-N species at binding energy (BE) of 399.0 eV, Mn-C-N at BE of 402.5 eV and N-H at BE of 401.1 eV, indicating the coordination of co-doped Mn, N with the matrix carbon. Meanwhile, no Mn and N could be detected from SC powder by XPS, further confirming the successful co-doping of Mn, N on the matrix. According to literatures, co-doped Mn and N could provide active sites to improve the ORR performance (Touach *et al.* 2016; Flegler *et al.* 2017).

To examine the ORR performance of Mn-N/SC and SC, LSV measurements have been carried out. As shown in Figure 4(a), the ORR overpotential of SC is significantly lower than that of carbon cloth, indicating the electrocatalytic activities of carbonized sewage sludge through proposed pyrolysis. Excitingly, the obtained Mn-N/SC catalyst exhibit excellent ORR activities, whose overpotential (0.3 V) and current density (0.8 A m^{-2}) is similar compared with commercial Pt/C. Moreover, the ORR peak potential of the Mn-N/SC electrode was observed was −0.2 V in Figure S4, which was more positive than the SC electrodes, showing that the Mn/N-SC had a high catalytic activity toward ORR. The dramatically enhanced ORR performance of SC after co-doping with Mn and N should be ascribed to coordination of Mn, N with graphitic carbon. Theoretically, Mn, N doping of carbon-based material could conjugate with π electrons of carbon to facilitate the adsorption of O_2 on the carbon-based material surface, thereby increasing ORR activity (Sun *et al.* 2012). In addition, Figure 4(a) shows the stability test of the Mn-N/SC catalyst using LSV. Obviously, the 1,000 cycle LSV plot only shifted about 10 mV in the negative direction compared to that of the pristine catalyst. Moreover, the stability of the Mn/N-SC was further evaluated during electrolysis by applying a constant potential of 400 mV in M9 solutions. As can be seen in Figure S5, the M-N/SC exhibit showed negligible decreases in current over a time span of 600 s, suggesting that Mn-N/SC has excellent electrocatalytic oxygen

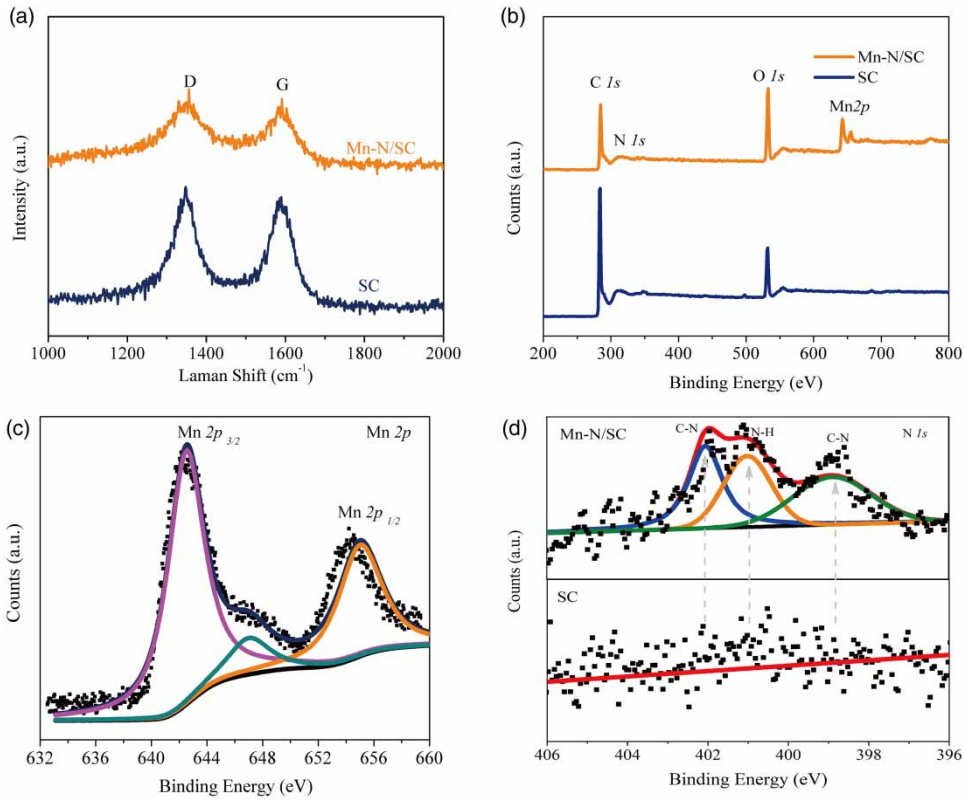

Figure 3 | (a) Raman spectra and (b) XPS spectrum of SC and Mn-N/SC. (c) Mn *2p* XPS spectrum of Mn-N/SC. (d) N *1s* XPS spectrum of SC and Mn-N/SC.

reduction stability, and meets the requirements of electrode large-scale applications.

To better understand the electrocatalytic activity of Mn-N/SC, we used RDE measurement to further investigate the ORR kinetics and mechanism. The number of electron transfer (n) was calculated by the Koutecky-Levich (K-L) equation, and J^{-1} was plotted against $\omega^{-1/2}$ at −0.8 V. The K-L equation was expressed as follows:

$$1/j = 1/(nAFkC_0)^{-1}/(0.62nAFD_0^{2/3}\upsilon^{-1/6}C_0\omega^{1/2})$$

The RDE data of Mn-N/SC at different rotation rates are depicted in Figure S6, from which we can observe that the current density is linearly related to the rotational speeds. The calculated n for Mn-N/SC was 3.19, which was consistent with previous research (Cao *et al.* 2016). The n of Mn-N/SC was close to a four-electron pathway, indicating that the ORR of Mn-N/SC is effective.

An excellent cathode electrode for MFC must have good electrical conduction, such as low impedance. Judged from EIS, the charge transfer resistances (Rct) of Pt/C and Mn-N/SC are similar, indicating the comparable oxygen reduction electron transfer ability of Mn-N/SC with commercial Pt/C, which is conducive to obtaining a high-power output in MFC. Accordingly, the high ORR activity and low resistance of Mn-N/SC indicate the alternative ORR catalyst derived from sewage sludge to replace the expensive Pt/C for applying microbial fuel cell.

To further evaluate and compare the ORR performance of fabricated sewage sludge cathode in MFCs, the power density measurements have been carried out (Figure 5(a) and 5(b)). As shown in Figure 5(a), the MFC with the Mn-N/SC catalyst cathode obtained a power density of 1,120 mW m^{-2}, which is not significantly different from the power density of the MFC with the Pt/C cathode catalyst (1,240 mW m^{-2}), indicating the potential replacement of precious Pt in air-cathode single-chamber MFCs. Notably, the power density obtained by Mn-N/SC catalyst cathode was significantly higher than other reported MFCs with similar biochar cathode catalyst (Table 1). In addition, Figure 4(b) shows the individual potential curves for the cathodes and anodes. As shown in Figure 4(b), the anode potentials were almost the same, while the cathode potentials were significantly different, indicating that the catalytic activity of the cathode catalyst resulted in a difference in MFC performance. Meanwhile, the cathode

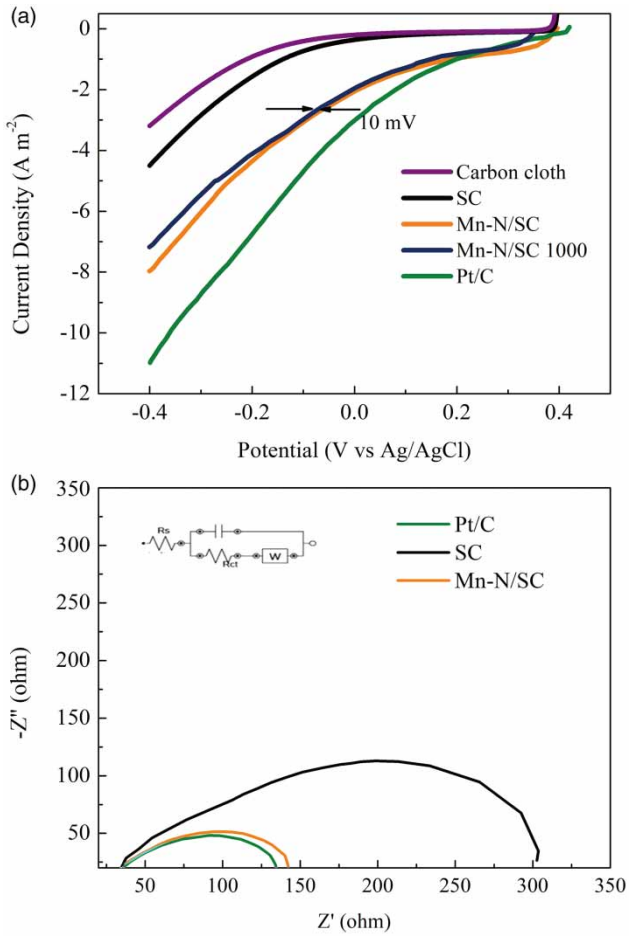

Figure 4 | Electrochemical performances of different catalysts (reference electrode: Ag/AgCl). (a) LSV curves of carbon cloth, SC, Mn-N/SC and Pt/C from 0.4 to −0.4 V (Scan rate. 5 mV s^{-1}). (b) EIS of SC, Mn-N/SC and Pt/C.

equipped with Mn-N/SC achieved a high potential, which is very advantageous for the ORR because more active sites were available for O_2 reduction. The power density results revealed that the fabricated Mn-N/SC derived from sewage sludge was a promising catalyst for MFC to replace expensive commercial Pt/C catalyst.

Cost comparisons of Mn-N/SC catalyst were further investigated. The total cost of Mn-N/SC preparation was about 26 US$ kg^{-1}, including 22 US$ kg^{-1} for carbonation processes and 4 US$ kg^{-1} chemical reagent costs (Yuan *et al.* 2015). This cost was much lower than 25,000 US$ kg^{-1} required for the commercial Pt/C and similar wood-based biomass carbon catalysts (20 US$ kg^{-1}) (Huan *et al.* 2014). Moreover, the conversion of SS into advanced catalyst materials in MFCs in a simple step in this study reduced its original disposal cost and avoided secondary sludge.

CONCLUSION

In this case, we have proposed and proved a new strategy to convert hazardous sewage sludge waste into efficient ORR electrocatalysts. The sewage sludge was first converted into porous carbon materials. Then, Mn and N species were uniformly doped on the carbonized sewage sludge matrix to further improve its ORR catalytic performance. The well-constructed M-N/SC catalyst demonstrates high formation turns over frequency and low ORR overpotential, which could be comparable with commercial expensive Pt/C catalyst. Considering the simple operation, significant cost-saving and easy scale-up, this facile strategy to convert hazardous sewage sludge waste into efficient ORR electrocatalyst provides a promising yet practical solution for green organic pollutant treatment.

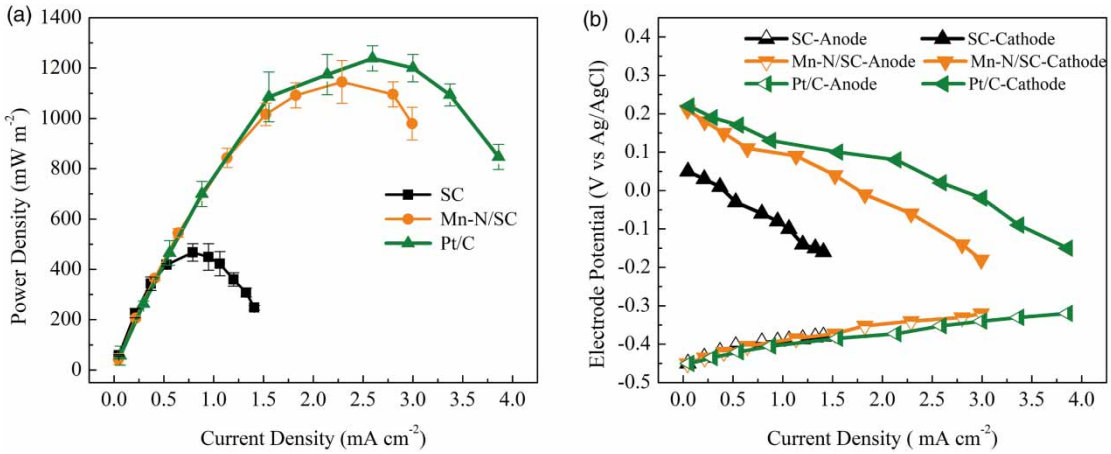

Figure 5 | Performances of MFC equipped with different cathodes (SC, Mn-N/SC, and Pt/C). (a) Polarization curves of MFC with different cathodes; (b) individual potentials of the electrodes in the MFCs.

Table 1 | Power densities generated by different cathode catalyst

Cathode catalyst	Microorganism	Power density (mW m^{-2})	Catalyst: Pt/C	Reference
Mn-N/SC	Mixed	1,120 ± 94	0.97	This study
Wood-based biomass	Mixed	606		Huggins *et al.* (2015)
Banana-based biochar	*Escherichia coli*	528	0.76	Huan *et al.* (2014)
Sewage sludge biochar (700 °C)	Mixed	517	0.82	Yuan *et al.* (2013)
Sewage sludge biochar	Mixed	969	0.90	Yuan *et al.* (2015)

NOTES

The authors declare no competing financial interest.

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SUPPLEMENTARY MATERIAL

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