Packed anode derived from cocklebur fruit for improving long-term performance of microbial fuel cells

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ABSTRACT Packed anode of microbial fuel cells (MFCs), commonly with a dense structure, suffers from the clogging, resulting in unsatisfied long-term stability of MFCs. Herein, we fabricate a biochar-based packed anode with a loose structure to enhance the long-term performance of MFCs equipped with packed anodes. The biochar, derived from cocklebur fruit, endows the packed anode with a loose structure but excellent conductivity. Once incorporated into MFCs, the biochar-based packed anode can yield comparable performance to benchmark materials. Particularly, the biochar-based MFCs present no obvious decrease of the power output during 150 days' operation, which is attributed to the clogging-resistant effect induced by the loose structure of biochar-based anode. The cocklebur fruit-derived biochar can be a promising candidate for MFC anodes, and should facilitate both scaling-up and practical applications of MFCs.

Keywords: microbial fuel cells, biochar, cocklebur fruit, packed anode, long-term stability

INTRODUCTION

Microbial fuel cells (MFCs) have received increasing interest as promising devices for electricity production and simultaneous wastewater treatment [1,2]. In an MFC system, the exoelectrogens grow on the anode and oxidize organic matters to generate electrons that then travel from the external circuit to electron-accepting cathode, thus generating electricity. In view of electron generation, the performance of MFCs is highly influenced by the anode as a host for exoelectrogen biofilms, and therefore the anode of MFC has attracted continuous attention [3].

Recently, anodes with different structures based on

various materials have been investigated in MFCs [4]. Standalone anodes are the common choice in MFCs, which can be fabricated by planar materials (carbon cloth/paper/plate, stainless steel mesh, Ti plate, etc.) [5,6] and three-dimensionally structured materials (carbon brush, graphene sponge, polymer-based textile, etc.) [5,7,8]. In addition to standalone anodes, the packed anode is another type of anode for MFCs, possessing several advantages such as low cost and feasibility for scaling up [9,10]. For example, packed anodes, made of granular graphite [11], granular activated carbon [9], and carbonized natural materials [12,13], can yield satisfactory electricity-generating performances with low overall cost of MFCs.

In the packed anodes, the materials commonly need to be densely packed for conductive contact [14], and therefore the reduced space among the packing materials, especially when the size of material is down to several millimeters. Unfortunately, such dense packing gives rise to clogging, either from continuous biofilm growth or particles originally from wastewater, which hinders the long-term stability of MFCs [15]. To minimize the clogging, some packing materials have been explored. A graphite coated crumb rubber, derived from recycled tire, has been used as a packed anode with good electricity-generating performance. The light weight of rubber particle reduces both clogging and cost, but posts challenges in conductive connection among the rubber particles [16]. Suitable packing materials are highly desired for fabricating packed anodes with good electricity-generating performance and long-term stability.

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Cocklebur, native to the Americas and eastern Asia, is a genus of flowering plants that has large plantation areas around the world. Cocklebur fruit is a hard, oval/globose double-chambered and single-seeded bur (0.81–2.01 cm) with rough and prickly surface. When packed tightly, the contact between cocklebur fruits can be ensured by the extended thorns with a relatively loose structure. Inspired by the unique morphology of cocklebur fruits, we transformed the cocklebur fruits into conductive biochar by carbonization, as a promising candidate for packed anode in MFCs.

In this study, biochar derived from cocklebur fruits by direct carbonization was fabricated as a packed anode for MFCs. Compared with the MFCs based on benchmark materials (granular activated carbons), the MFCs fabricated with cocklebur fruit-derived biochar, can achieve comparable electricity-generating performance and give steady power output even after 150 days. The long-term stability should be mainly attributed to the loose structure of the biochar-based packed anode, which can resist clogging during the operation of MFCs. Considering the satisfactory electricity generation and excellent stability, we believe that this cocklebur fruit-derived biochar can facilitate practical applications of MFCs with large-scale reactors for long-term operation in the future.

EXPERIMENTAL SECTION

Preparation of carbon materials

Raw cocklebur fruits were obtained from taobao.com (Shop id: 511734209). The cocklebur fruits were washed with deionized water and air dried, and then they were carbonized into biochar in a high-temperature furnace at 900°C for 3 h under a N₂ atmosphere without any pre- or post-treatment. The carbonized cocklebur fruit was addressed as “biochar” in this work.

Two types of commercially available granular activated carbons, activated charcoal and activated coke, were purchased from taobao.com (Shop id: 112323529 and 102258439), and utilized as benchmark materials for packed anodes in MFCs. It should be noted that activated charcoal was derived from fruit (walnut/peach/apricot) shells and activated coke was derived from coal. Both types of granular activated carbons were immersed in 0.1 mol L⁻¹ HCl overnight, washed with deionized water till neutral pH, dried at 60°C and then packed as anodes.

Microbial fuel cell setup and operation

A single-chamber MFC, with a liquid volume of 450 mL,

was fabricated by a cuboid plastic bottle. The anode of the MFC was obtained by packing carbon materials tightly into a stainless steel mesh cylinder (about 45 cm³). Air-cathode, applied in the single-chamber MFC, was made by a hydrophobic carbon cloth (5 cm×5 cm) which was firstly coated with four diffusion layers on one side and then coated with platinum/carbon black (Pt/C) catalyst on the other side. For the fabrication of each diffusion layer, 20% polytetrafluoroethylene (PTFE, DuPont, USA) was spray coated, dried naturally and subsequently annealed at 370°C for 30 min, resulting in a PTFE loading amount of around 10 mg cm⁻². For Pt/C catalyst coating on the other side, an ethanol dispersion (1.5 mL), containing 20 mg Pt/C catalyst (20 wt% Pt content, Johnson Matthey, USA) and 140 μL 2 wt% PTFE, was spray-coated and annealed at 370°C for 30 min, forming a catalyst layer. The resulting carbon cloth-based cathode contained about 0.65 mg cm⁻² Pt/C catalyst [17]. The MFC was constructed with a packed anode in the anode chamber, and an air-cathode directly exposed to air, making it a membrane-less single-chamber MFC. Experiments were performed in triplicate to evaluate each carbon material.

The MFC reactors were inoculated with inoculum from the anolyte (originally inoculated with activated sludge) of another well-running single-chamber MFC and operated in a close circuit mode with an external resistor of 1 kΩ. Briefly, 50 mL inoculum was mixed with 400 mL artificial wastewater, and filled into MFC reactor. The mixture of inoculum and artificial wastewater was fed for two cycles, and from the third cycle on, 450 mL artificial wastewater was refilled when the voltage across external resistor dropped to about 50 mV. The artificial wastewater was a mixture of CH₃COONa (1 g L⁻¹), NaH₂PO₄·2H₂O (2.46 g L⁻¹), Na₂HPO₄·12H₂O (11.40 g L⁻¹), NH₄Cl (0.31 g L⁻¹), KCl (0.13 g L⁻¹), a vitamin solution (5 mL L⁻¹), and a mineral solution (12.5 mL L⁻¹) [18]. Temperature of the MFCs was controlled at 30±4°C [19].

Carbon material characterization

Thermogravimetric analysis (TGA) was performed to characterize the carbonization of cocklebur fruit to biochar with a Netzsch STA-499 F3 at N₂ atmosphere. Powder X-ray diffraction (XRD) measurement for the carbon materials was carried out on a Rigaku Smartlab (9 kW) X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å) at room temperature. Raman spectra were collected by a confocal microscope Raman spectrometer system (Witec Alpha 300). Sheet resistance of the materials was measured using a ST2253 digital four-point

probe (Suzhou Jingge Electronic Co., Ltd., China). It should be noted that the three types of carbon materials for packed anode were ground before resistance measurement. The Brunauer-Emmett-Teller (BET) surface area and pore size were obtained from N_2 adsorption-desorption isotherms at -196°C (77 K) by an ASAP 2460 analyzer (Micromeritics). Scanning electron microscopy (SEM) was performed on JEOL JSM-7800F, and the elemental analysis was achieved using energy-dispersive X-ray spectroscopy (EDX). To obtain SEM images of biofilms attached on the carbon materials, the carbon materials collected from MFC anodes were firstly immersed into glutaraldehyde solution (3 wt%, 0.5 h), followed by washing three times with 0.2 mol L^{-1} phosphate buffer saline (pH 6.8). The carbon materials were then dehydrated stepwise in a

series of ethanol/water solutions (ethanol concentration: 50%, 70%, 80%, 90%, and 100%) and dried in a desiccator prior to SEM analysis at room temperature. Chemical oxygen demand (COD) of artificial wastewater was measured with a 6B-100 multimeter (Jiangsu ShengAo-hua Environment Protection Technology Co. Ltd, China) after digestion with the COD kit in a 6B-12 digester according to the protocol in the manual.

Electrochemical measurements

The close circuit voltage of MFCs was recorded, over a $1\text{ k}\Omega$ external resistor, by a data acquisition system (Yavii YAV, 16 CE, China). After stabilization, polarization curves were obtained by linear sweep voltammetry at a low scan rate of 0.1 mV s^{-1} [20,21], using a CHI 630E electrochemical workstation (Chenhua Instruments Co., Ltd., China), with a 2-electrode setup (working electrode: MFC cathode, counter and reference electrode: MFC anode). Electrochemical impedance spectroscopy (EIS) was carried out, when MFCs were at stable open circuit condition with fresh artificial wastewater, using a Zennium IM6 (Zahner) electrochemical workstation in the frequency range of 100 kHz – 10 mHz (amplitude: 5 mV) at 3-electrode mode (working electrode: MFC anode, counter electrode: MFC cathode, and reference electrode: $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$ (saturated)).

RESULTS AND DISCUSSION

Preparation and characterization of carbon materials

Carbonization of natural materials is a promising strategy for obtaining carbon materials from sustainable resources [22–24]. Complete carbonization of cocklebur fruit, as demonstrated by TGA curve (Fig. S1), can be achieved at 900°C to produce the biochar. After carbonization, the cocklebur fruit shrinks in size with a weight loss of $\sim 76.5\%$, while the unique shape of cocklebur fruit maintains well (Fig. 1a), which ensures further utilization in packed MFC anodes.

The powder XRD pattern of the biochar (Fig. 1b) possesses graphitic structure with the two characterization peaks, centered at $2\theta = 24^\circ$ and 44° , which can be assigned to the (002) and (101) diffraction planes of hexagonal graphite. The graphitic structure was also confirmed by the Raman spectrum (Fig. S2) with two bands at $\sim 1,358\text{ cm}^{-1}$ (D band, indicative of disordered microstructure in carbon materials) and $\sim 1,600\text{ cm}^{-1}$ (G band, indicative of graphitic carbon). In addition, the low intensity ratio of D-to-G bands (I_D/I_G) of around 1 indicates a relatively high graphitic degree and low

Figure 1 Preparation and characterization of biochar from cocklebur fruit. (a) Photos of a raw cocklebur fruit and a carbonized cocklebur fruit (biochar), (b) powder XRD pattern of the biochar, (c) SEM image of outer surface of the resulting biochar, and (d, e) enlarged SEM images of the rough surface (d) and a broken thorn (e) of the resulting biochar. Scale bars are 1 cm for (a), 100 μm for (c), and 10 μm for (d, e).

Figure 2 (a) Schematic diagram of packing carbon materials as MFC anodes, (b) time-dependent profiles of voltage generation for MFCs equipped with different anodes after initial inoculation (external resistance: 1 k Ω), (c) polarization and power curves of MFCs equipped with different anodes obtained by linear sweep voltammetry (scan rate: 0.1 mV s⁻¹).

disordered structure of the biochar [25]. In the SEM images (Fig. 1c, d), the biochar possesses rough outer surface with thorns all around, and pores in micrometer are inside the thorns (Fig. 1e). Further N₂ adsorption-desorption isotherms reveal that the biochar has a moderate BET surface area of 48.77 m² g⁻¹, and a pore volume of 0.023 cm³ g⁻¹ (Fig. S3). These results indicate that the biochar with graphitic and porous structure can be a good anode material for packed anode.

Similarly, both types of granular activated carbons were also characterized before incorporated into MFCs. After pre-cleaning (Fig. S4), the activated charcoal is black cylindrical granule, while the activated coke is irregularly-shaped granule with mainly black but minor rust color. Despite the slight difference in color, both of them possess the graphitic structure as indicated by the D and G bands in Raman spectra (Fig. S5) and characteristic peaks ($2\theta=24^\circ$ and 44°) in XRD patterns (Fig. S6). Different from cocklebur fruit derived biochar, both types of granular activated carbons, particularly the activated coke, contain impurities as confirmed by the unassigned peaks in XRD patterns and by further EDX analysis. As shown in Fig. S7, high content of metallic Fe (~15.3%) and other minor impurities (Ca, Mg, S, etc.) are found in activated coke, while minor impurities of Al, Si, S, etc. are observed in activated charcoal. The activated charcoal has irregular fragments on the surface (Fig. S8a,

b), exhibiting a moderate BET surface area of 80.00 m² g⁻¹ and a pore volume of 0.037 cm³ g⁻¹ (Fig. S9a, b). In contrast, activated coke presents fine microstructures with flake clusters on the surface (Fig. S8c, d), and its BET surface area is 330.18 m² g⁻¹ with a high pore volume of 0.19 cm³ g⁻¹ (Fig. S9c, d). All the three types of carbon materials give similar electric conductivity (Fig. S10).

Performance of microbial fuel cells equipped with different anodes

Biochar and the two types of granular activated carbons were packed tightly as the anodes, and tested in MFCs, respectively (Fig. 2a). After initial inoculation, repeatable cycles of voltage generation (~0.5 V) were obtained across external resistors of 1 k Ω for all the MFCs (Fig. 2b). Notably, the voltages of biochar-based MFCs rapidly reached 0.30 V at the 1st cycle (Fig. S11a) and 0.52 V at the 2nd cycle (~130 h), which was much faster than the granular activated carbon-based MFCs. As shown in the Fig. 2c and Table 1, the maximum power output of the biochar-based MFC was $572.57 \pm 24.90 \mu\text{W}$, which was similar to those of the activated charcoal and activated coke-based MFCs ($562.49 \pm 35.45 \mu\text{W}$ and $623.24 \pm 37.49 \mu\text{W}$). The cocklebur-derived biochar is a light-weight material. Among the maximum gravimetric power density of MFCs equipped with different anodes (Fig. S11b), the biochar-based anode presents a much

Table 1 Electricity generating performance of MFCs equipped with different anodes after reaching stable performance

Anodes	Weight (g)	Open circuit voltage (V)	Maximum power output (μW)	Maximum gravimetric power density ($\mu\text{W g}^{-1}$)	COD removal efficiency (%)
Biochar	4.07 ± 0.00	0.72 ± 0.02	572.57 ± 24.90	140.54 ± 6.19	75.63 ± 10.80
Activated charcoal	31.86 ± 0.44	0.71 ± 0.01	562.49 ± 35.45	17.64 ± 0.87	82.66 ± 4.15
Activated coke	18.82 ± 0.03	0.71 ± 0.00	623.24 ± 37.49	33.11 ± 1.96	82.10 ± 1.15

Figure 3 Characterization of biochar-based packed anodes in MFCs. Low magnified (a, c) and high magnified (b, d) SEM images of biofilm on the biochar surface and the exoelectrogens in the thorns. Equivalent circuit (e) and Nyquist plots (f) of different anodes in MFCs measured by a 3-electrode mode with the amplitude of 5 mV and the frequency range of 100 kHz–10 mHz (dots: experimental data, line: stimulated curve based on the equivalent circuit in 3e). Scale bars are 10 μm for (a, c) and 1 μm for (b, d); R_{ohm} is ohmic resistance of electrode, R_{bio} and CPE_{bio} are the ohmic resistance and constant phase element of the biofilm, R_p and CPE_{dl} are the polarization resistance and constant phase element of the double layer, and W represents Warburg element related to diffusion.

higher value ($140.54 \pm 6.19 \mu\text{W g}^{-1}$) than the anodes fabricated by activated charcoal ($17.64 \pm 0.87 \mu\text{W g}^{-1}$) and activated coke ($33.11 \pm 1.96 \mu\text{W g}^{-1}$). These results indicate that the biochar can yield good performance in power generation when used as a packed anode in MFCs.

Characterization of microbial fuel cell anodes

Biofilm formation is crucial for electricity generation in MFCs. Therefore, after MFCs reach stable performance, we checked the biofilm on biochar and activated carbon granules by SEM. The sampling positions of carbon materials were limited in the outmost layers of the packed anodes to minimize the change brought to the anode packing and damage to biofilms. As shown in Fig. 3a, b, a dense biofilm was observed on the rough surface of the biochar with full coverage. Moreover, exoelectrogens were even found in the inner surface of the pores in the thorns (Fig. 3c, d). By contrast, the coverages of biofilms for granular activated carbons are relatively low (Fig. S12). The favored biofilm growth on biochar can be attributed to the good biocompatibility of biochar. On the other

hand, the granular activated carbons have higher packed weight and higher BET surface area than biochars, providing more space for biofilm formation despite a small portion of inaccessible micropores. Accordingly, we deduce that the total amount of biofilms on granular activated carbon-based anodes could reach a comparable level with that of biochar-based anode, providing comparable electron-generating abilities in MFCs. Therefore, despite the differences of biofilm observed by SEM, MFCs equipped with the three different types of anodes still can provide comparable electron-generating abilities.

EIS was carried out at a 3-electrode mode to characterize the MFC anodes. As shown in Fig. 3e, f, low ohmic resistances of all the anodes ($<10 \Omega$) indicate good conductive contact of the packed structure. Meanwhile, the polarization resistance of the activated coke-based anode is the lowest, possibly because Fe-containing species encourage the exoelectrogens to release flavins as an electron transfer mediator and thus accelerate the electron transfer kinetics [26,27]. Consistently, activated coke-based MFC yields slightly higher power output than

biochar and activated charcoal-based MFCs. We can conclude that when applied as a packed anode in MFC, despite different features in biofilm formation and electron transfer kinetics, cocklebur fruit-derived biochar can achieve satisfactory electricity-generating performance compared with the benchmark activated carbon materials.

Long-term performance of microbial fuel cells

In addition to the evaluation of MFC power output, the stability of MFCs equipped with different anodes was examined after operation for 150 days. Inspiringly, the biochar-based membrane-less single-chamber MFCs did not exhibit any decrease in terms of maximum power output, and maintained excellent repeatability even after 150 days (Fig. 4a). By contrast, the performance of most granular activated carbon-based MFCs deteriorated unrepeatably to different extents, with one of them even not generating any power (Fig. S13). The actual volume of packed anodes was measured by a water displacement method to investigate this variation. Despite the same apparent volume of $\sim 45 \text{ cm}^3$ for all the three anodes, the actual solid volume of biochar, which had oval shape and extended thorns, was only $\sim 10 \text{ cm}^3$ (22%), leaving $\sim 35 \text{ cm}^3$ (78%) as free space. In stark contrast, the actual volumes of both granular activated carbons were much higher, leaving less free space (Fig. 4b). Benefiting from the large free space, we believe that the biochar-based packed anode with a loose structure can facilitate biochar-solution contact and make the anode more resistant towards clogging caused by biofilm growth and particles from wastewater [2], thus ensuring the long-term stability of MFCs.

We sampled the biochar and carbon granules from both the outmost layer and the inner positions of the packed anodes for biofilm observation. On the biochars, sampled from both the outmost and inner positions, thick biofilms indicate homogenous biofilm formation in the whole packed anode. Differently, for both types of carbon granules, thick biofilms were only observed on those granules sampled at the outmost layer. For granules sampled from the inner position of the packed anodes, only scattered exoelectrogens were observed on the surface (Fig. S14). These observations reveal that in densely packed anodes the biofilm on the outmost-layer carbon granules hinders exoelectrogens from entering into the inner structure of the packed anode (known as clogging effect). Consequently, MFCs equipped with densely packed anodes typically exhibit deterioration of long-term stability in an unrepeatable way. By contrast,

Figure 4 Long-term performance of biochar-based MFCs and volume distribution for various packed anodes. (a) Polarization and power curves of biochar-based MFCs obtained by LSV after 150 days' operation. (b) Volume distribution for anodes packed with different carbon materials.

the biochar-based packed anodes with a loose structure allow continuous biofilm growth on all the exposed surface, possibly reaching a balance between exfoliation of dead exoelectrogens and growth of active exoelectrogens. In this way, the excellent stability of the biochar-based MFC can be guaranteed in the membrane-less MFC. Despite varied chemical compositions in real wastewater, the biofilm evolution process is similar to that in the current study, and therefore we think that this packed anode with a loose structure could shed light on practical long-term operation of MFCs [28].

Considerations on the economic and environmental effects

MFC has been viewed as a promising technology to harvest chemical energy from wastes. However, the capital cost, in which electrodes contribute to a large content (20%–50%) [12], remains too high for wide applications. Granular activated carbon is considered as a cost-effective anode candidate in a packed structure compared with conventional standalone carbon materials. In order to achieve comparable power output, the biochar, developed herein as packed anode, requires similar cost to granular activated carbon (Table S1). In addition, the excellent long-term stability of biochar-based packed anode would reduce maintenance cost [17], like the cost for replacing anode.

Regarding the environmental impacts, the one-step carbonization avoids further activation which typically requires chemical additives or further thermal energy consumption. Moreover, the biochars for MFC anode have the potential to be reused. For example, the lightweight material with mature biofilms can be used as a biofilm carrier in wastewater treatment processes, presenting positive environmental effects [29]. The cocklebur fruit-derived biochar, with excellent performance and low cost, can be a suitable anode candidate for large-scale MFCs.

CONCLUSIONS

Here the cocklebur fruit-derived biochar was used to fabricate packed anode for MFCs. Remarkably, the biochar-based anode has superior stability, for more than 150 days, and comparable electricity-generating performance to those of the anodes packed with benchmark granular activated carbons. Our study reveals that the long-term stability of biochar-based anode should be mainly due to its clogging-resistant loose structure. Considering the excellent performance and low cost of the cocklebur fruit-derived biochar, we believe that this study could facilitate practical applications of MFCs with large-scale reactors and long-term operation in the future.

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- Logan BE, Rabaey K. Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. *Science*, 2012, 337: 686–690
- Sun M, Zhai LF, Li WW, *et al.* Harvest and utilization of chemical energy in wastes by microbial fuel cells. *Chem Soc Rev*, 2016, 45: 2847–2870
- Lu M, Qian Y, Huang L, *et al.* Improving the performance of microbial fuel cells through anode manipulation. *ChemPlusChem*, 2015, 80: 1216–1225
- Li S, Cheng C, Thomas A. Carbon-based microbial-fuel-cell electrodes: from conductive supports to active catalysts. *Adv Mater*, 2017, 29: 1602547
- Ci S, Cai P, Wen Z, *et al.* Graphene-based electrode materials for microbial fuel cells. *Sci China Mater*, 2015, 58: 496–509
- Xie Y, Ma Z, Song H, *et al.* Melamine modified carbon felts anode with enhanced electrogenesis capacity toward microbial fuel cells. *J Energy Chem*, 2017, 26: 81–86
- Pang S, Gao Y, Choi S. Flexible and stretchable microbial fuel cells with modified conductive and hydrophilic textile. *Biosens Bioelectron*, 2018, 100: 504–511
- Tao Y, Liu Q, Chen J, *et al.* Hierarchically three-dimensional nanofiber based textile with high conductivity and biocompatibility as a microbial fuel cell anode. *Environ Sci Technol*, 2016, 50: 7889–7895
- Jiang D, Li B. Granular activated carbon single-chamber microbial fuel cells (GAC-SCMFCs): A design suitable for large-scale wastewater treatment processes. *Biochem Eng J*, 2009, 47: 31–37
- Wu S, Li H, Zhou X, *et al.* A novel pilot-scale stacked microbial fuel cell for efficient electricity generation and wastewater treatment. *Water Res*, 2016, 98: 396–403
- Rabaey K, Clauwaert P, Aelterman P, *et al.* Tubular microbial fuel cells for efficient electricity generation. *Environ Sci Technol*, 2005, 39: 8077–8082
- Huggins T, Wang H, Kearns J, *et al.* Biochar as a sustainable electrode material for electricity production in microbial fuel cells. *Bioresource Tech*, 2014, 157: 114–119
- Zhou Y, Zhou G, Yin L, *et al.* High-performance carbon anode derived from sugarcane for packed microbial fuel cells. *Chem-ElectroChem*, 2017, 4: 168–174
- Logan BE. *Microbial Fuel Cells*. Hoboken: John Wiley & Sons, Inc., 2007
- Rabaey K, Clauwaert P, Aelterman P, *et al.* *Bioelectrochemical Systems: From Extracellular Electron Transfer to Biotechnological Application*. London: IWA Publishing, 2009
- Wang H, Davidson M, Zuo Y, *et al.* Recycled tire crumb rubber anodes for sustainable power production in microbial fuel cells. *J Power Sources*, 2011, 196: 5863–5866
- Lu M, Qian Y, Yang C, *et al.* Nitrogen-enriched pseudographitic anode derived from silk cocoon with tunable flexibility for microbial fuel cells. *Nano Energy*, 2017, 32: 382–388
- Lovley DR, Phillips EJP. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Appl Environ Microbiol*, 1988, 54: 1472–1480
- Liu L, Tsyganova O, Lee DJ, *et al.* Anodic biofilm in single-chamber microbial fuel cells cultivated under different temperatures. *Int J Hydrogen Energy*, 2012, 37: 15792–15800
- Velasquez-Orta SB, Curtis TP, Logan BE. Energy from algae using microbial fuel cells. *Biotechnol Bioeng*, 2009, 103: 1068–1076
- Feng C, Lv Z, Yang X, *et al.* Anode modification with capacitive materials for a microbial fuel cell: an increase in transient power or stationary power. *Phys Chem Chem Phys*, 2014, 16: 10464–10472
- Hu B, Wang K, Wu L, *et al.* Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv Mater*, 2010, 22: 813–828
- Imtiaz S, Zhang J, Zafar ZA, *et al.* Biomass-derived nanostructured porous carbons for lithium-sulfur batteries. *Sci China Mater*, 2016, 59: 389–407
- Jian M, Wang C, Wang Q, *et al.* Advanced carbon materials for flexible and wearable sensors. *Sci China Mater*, 2017, 60: 1026–1062
- Chen S, Tang J, Jing X, *et al.* A hierarchically structured urchin-like anode derived from chestnut shells for microbial energy harvesting. *Electrochim Acta*, 2016, 212: 883–889
- Marsili E, Baron DB, Shikhare ID, *et al.* *Shewanella* secretes flavins that mediate extracellular electron transfer. *Proc Natl Acad Sci USA*, 2008, 105: 3968–3973
- Wu D, Xing D, Lu L, *et al.* Ferric iron enhances electricity generation by *Shewanella oneidensis* MR-1 in MFCs. *Bioresource Tech*, 2013, 135: 630–634
- Li WW, Yu HQ, He Z. Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. *Energy Environ Sci*, 2014, 7: 911–924
- Mao Y, Quan X, Zhao H, *et al.* Accelerated startup of moving bed biofilm process with novel electrophilic suspended biofilm carriers. *Chem Eng J*, 2017, 315: 364–372

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary materials are available in the online version of the paper.

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基于苍耳子的堆积型疏松阳极用于提升微生物燃料电池的长期运行性能

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摘要 基于堆积型阳极的微生物燃料电池因材料成本低且在大型反应器中适用性强, 在实际应用中具有较好前景. 但是, 堆积结构常带来堵塞问题, 因此基于堆积型阳极的微生物燃料电池通常稳定性较差. 本文中, 我们用生物炭堆积的疏松阳极来提升堆积型阳极微生物燃料电池的长期稳定性. 生物炭由苍耳子直接炭化获得, 保持了苍耳子特殊的外形, 保证了其在制备成堆积型阳极后具有疏松的结构和良好的导电性. 用于微生物燃料电池时, 该生物炭堆积型阳极获得了与常用的活性炭材料堆积阳极相当的产电性能, 且该燃料电池在150天的运行时间内产电性能无明显下降, 而作为参照的活性炭堆积阳极燃料电池的性能呈现极大下降. 这种良好的稳定性是因为生物炭堆积阳极的疏松结构减少了长期运行过程中的堵塞现象. 这种基于苍耳子的生物炭材料可以作为高效稳定的微生物燃料电池阳极材料, 有望在实际应用中大型化长期运行.