Int. J. Electrochem. Sci., 13 **(2018)** 461 – 471, doi: 10.20964/2018.01.28

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Production of Electricity from Rice Straw with different Pretreatment Methods Using a Sediment Microbial Fuel Cell

Tian-shun Song[1,2,3,4], *Shuai Hou*[1,3], *Jiguang Zhang*[1,3], *Haoqi Wang*[1,3], *Jingjing Xie*[1,2,3,4,*]

[1] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 211816, PR China
[2] CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China
[3] College of Life Science and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, PR China
[4] Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing 211816, PR China
[*]E-mail: xiej@njtech.edu.cn

Received: 7 September 2017 / *Accepted:* 31 October 2017 / *Online Published:* 1 December 2017

The purpose of this study is to improve the performance of solid phase microbial fuel cells (SMFC) by pretreating straw with several reagents (H_2SO_4, NaOH and H_2O_2). Electrochemical performance and straw properties were measured. The results show that when compared with the control group (untreated rice straw), the SMFC with rice straw after hydrogen peroxide pretreatment (SMFC-H_2O_2) and the SMFC with rice straw after sulfuric acid pretreatment (SMFC-H_2SO_4) lasted more than 6 to 8 days under high voltage (higher than 500 mV). Furthermore, an SMFC with rice straw after sodium hydroxide pretreatment (SMFC-NaOH) can last more than 22 days under high voltage, which is almost twice the endurance of the control group. The maximum power density of the SMFC-NaOH was 140 mW/m^2 on day 50, which was 3.6 times that of the control. Therefore the NaOH pretreatment worked in favor of rice straw biodegradation by anaerobic microorganisms and extended the sustained discharge time of the SMFC.

Keywords: Straw resource utilization; Electricity; Long discharge; Cellulose; Pretreatment

1. INTRODUCTION

SMFC is a type of MFC configuration, which [1] harvests electricity from solid phase organic matter, such as sludge, sediment and soil [2-5]. In this configuration, the cathode is commonly suspended in the aerobic water, while the anode is embedded in anaerobic solids, at the bottom of the cell [6]. SMFCs can be used as power sources for instruments, deployed in marine and lake environments, for long-term monitoring [7-9], due to their simple design and the rich, solid-phase, organic matter available in these environments. In addition, SMFC can perform in situ bioremediation of this organic matter and accelerate the removal of these organics (even refractory organic matter) [10-12].

The low mass transfer rate, in the anode region [13, 14], is one of the important limiting factors for SMFCs, leading to limited output power and short sustained discharge time. Several approaches have been demonstrated for improving the mass transfer rate in the anode region, by addition of plant rhizodeposits [15] or biomass, such as chitin or cellulose [16, 17]. Among these, cellulose is the structural component of the primary cell walls of green plants, dead leaves and stems of plants, such as straw [4] which can also be added to improve SMFC performance. Straw comprises the largest fraction of agricultural waste in many countries, especially in China. Most of the straw is commonly used as mulch or fodder and the rest is burnt or left unused. Therefore, using straw as the substrate of an SMFC, for power generation, provides us with an innovative solution for the treatment of this straw waste.

Straw contains a high percentage of lignin, which is hardly biodegradable by anaerobic microorganisms [18]. However, the crystalline structure and available surface area of lignocellulosic materials make the anaerobic process difficult, because the enzyme cannot reach the reaction sites, unless the lignocellulosic structure is opened. Thus, pretreatment is required to improve the anaerobic process, by changing the structure of the straw. Various methods for pretreatment of these agricultural residues have been studied, including mechanical, thermal, chemical (i.e. alkali, acidic, oxidative) and biological methods [19]. These pretreatment methods result in improvements to the subsequent enzymatic hydrolysis. Nevertheless, most of these studies have been performed in connection with ethanol or biogas production. For example, acid pretreatment can cut the long chains of cellulose and most of the hemicellulose is removed. It has been reported that acid pretreatment of rice straw produces 66.79% of the theoretically expected ethanol yield [20]. NaOH was found to be one of the most effective alkaline reagents for removal of lignin. It has been reported that a 72.9% increase in total biogas production was achieved with straw, treated with a 2.0% solution of NaOH [21]. Rice straw can use as substrate for electricity in MFC [22]. However, few studies have focused on the effects of straw, using various pretreatment methods, on SMFC performance.

In this study, three different types of reagents (acid, alkali and hydrogen peroxide) were used in the pretreatment of rice straw, to evaluate their effects on the performance of the SMFC. All the SMFCs operated for two months. The performance differences of these SMFCs are explained through in-depth analyses.

2. MATERIALS AND METHODS

2.1. SMFC construction and operation

The soil (0-10 cm depth) was obtained from woodland within Nanjing Tech University, China, and passed through a 0.5 cm sieve to remove coarse debris. The soil water content was 53 %. The loss on ignition (LOI) of the soil was 6.4%. The SMFCs were made of plexiglass, with internal chamber dimensions of 110 mm diameter and 150 mm height. 3.5 g of straw (0.6% of the precipitate's dry weight) was added to 600 g of wet soil. Stirred evenly. All experimental groups were set up in duplicates, and the experimental group without straw was set up as control. Water loss via evaporation during the operation was routinely replenished with tap water to maintain water level above the cathode electrode 2cm or so. Unless otherwise stated, no additional substances are added. The electrodes used in this experiment (the same cathode anode electrode) were carbon felt (5 cm * 20 cm * 0.3 cm. The size of this anode was 200 mm× 50 mm×30 mm (length × width × thickness), to minimize mass transfer limitation within the soil, as well as to increase the opportunities for contact between the soil and anode. Each anode was placed along a polyvinyl chloride cylindrical holder (31.8 cm^2 based on electrode footprint area), with the cathode (54 cm^2) floating above the water. The SMFCs were operated at a fixed external resistance of 1000 Ω and maintained at 25 ℃.

2.2. Pretreatment of rice straw

Rice straw was collected locally and cut into 10 mm × 5 mm pieces. For the acid pretreatment, 10 g of rice straw was added to each of the 1000 mL beakers, which were each then filled with 200 ml of sulfuric acid (3%). The wet rice straw, in the beakers, was shaken for 24 h, at 37 ℃, and washed with distilled water, until the pH of the wash solution was neutral, then dried at 60 ℃, and subsequently added to the anode chamber of the SMFC-H_2SO_4. For the alkali and the hydrogen peroxide pretreatments, 10 g of rice straw were added to 1000 mL beakers, which were then filled with 200 ml sodium hydroxide (5%) and hydrogen peroxide (3%), respectively. The next steps were the same as for the acid pretreatment, and then added to the anode chambers of the SMFC-NaOH and the SMFC-H_2O_2.

2.3. Analysis

The voltages produced by the SMFCs, during the experiments, were recorded at intervals of 30 minutes, using a precision multimeter and a data acquisition system (Keithley Instruments 2700, USA). The external resistor was varied over the range of 50-2000 Ω to obtain polarization curves. Voltage was converted to power density, based on the footprint area of the anode [6]. Internal resistance was calculated via the polarization slope method [23]. The Ag/AgCl reference electrode was positioned near the cathode, to measure the cathode redox potential. Anode redox potentials were approximated by subtracting the cell potentials from the cathode redox potentials. The LOI of the soil was determined by weighing the sample before and after combustion at 550℃ for 4 h [12]. The surface morphologies of rice straws were studied, using a scanning electron microscope (SEM) (JSM-5900, Japan). The cellulose, hemicellulose and lignin of their biomass were analyzed according to the methods described by Ziaie-Shirkolaee et al. [24].

3. RESULTS AND DISCUSSION

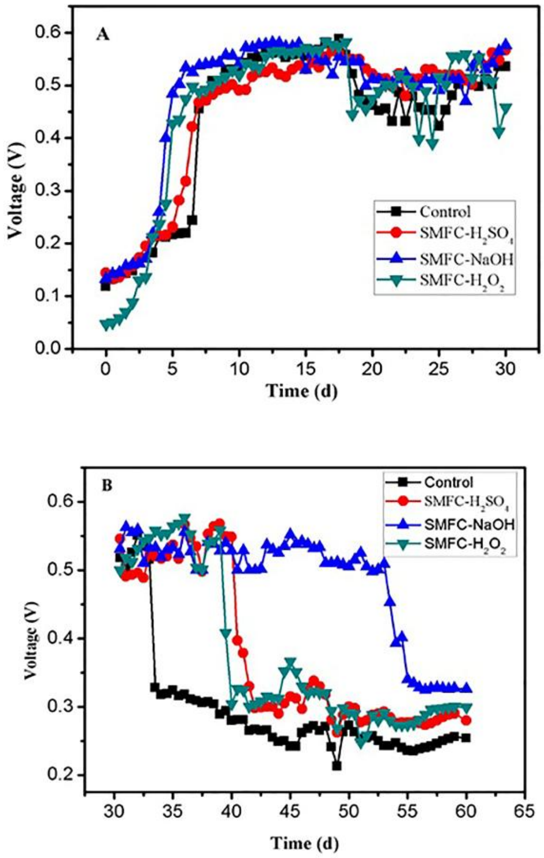

Figure 1. Voltage generation produced by the SMFCs with rice straw, after pretreatment with different reagents. (A)0-30 days and (B) 30-60 days

3.1. Electricity generation from SMFCs

SMFC production performance has been significantly improved after adding the pretreated straw. During the first 3 days of operation, the voltages from the pretreated SMFCs were low and the voltage of SMFC-H_2O_2 was even lower than that of the other SMFCs (Figure 1A). This phenomenon might be due to the formation of an electrochemically active biofilm on the anode surfaces during the initial reaction phase and rice straw, with various pretreatments, may affect the rate of biofilm formation in the anode [25]. The voltage of these SMFCs increased quickly afterwards, with the fastest growth of voltage displayed by the SMFC-NaOH, followed by the SMFC-H_2O_2 and the SMFC-H_2SO_4. The growth of voltage in the control was the lowest. The results implied that the various pretreatments of the rice straw were beneficial to the growth of SMFC voltage. Adding rice straw into soil can facilitate the release of dissolved organic matter in soil to produce more electricity after electrochemically active biofilm formation, rice straw after NaOH treatment may release more dissolved organic matter, thus accelerated the growth of the voltage in SMFC-NaOH. Ten days later, the voltage of the pretreated SMFCs became stable (about 530 mV), with the differences among the voltages produced by all the SMFCs not being very significant, during 30 days of operation.

30 days later, all the SMFCs were still stable (Figure 1B), the voltage of the control declined to 318 mV on day 34. This was the first voltage drop shown by any of the SMFCs. But later, a similar phenomenon was observed in other SMFCs. The phenomenon of maintaining high voltage was obvious in the SMFC-NaOH, where the voltage of the SMFC-NaOH declined rapidly until day 56, which was almost 2 times the number of days, when compared to the control. Until the end of the experiment, the voltage of the control group was 254 mV, while those of the SMFC-H_2SO_4 and the SMFC-H_2O_2 were 280 mV and 299 mV, respectively. The SMFC-NaOH still had the highest voltage at 326 mV.

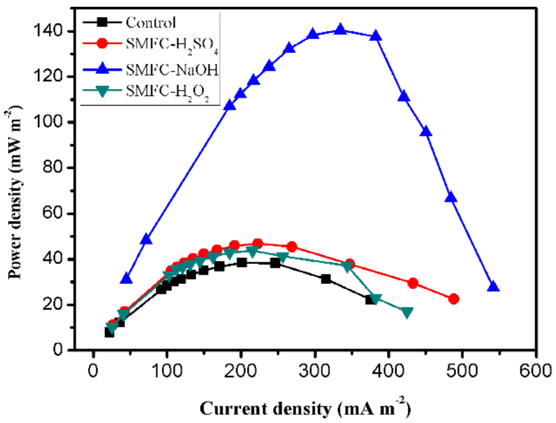

Figure 2. Power curves collected for the SMFCs with rice straw, after pretreatment with different reagents, on day 50.

The maximum power density (P_{max}), as functions of current density power curves for the different SMFCs, were obtained, as shown in Figure 2, on day 50. All the P_{max} values of the SMFCs with rice straw pretreatment were higher than that of the control (38 mW/m^2), with the P_{max} of the SMFC-NaOH at 3.6 times that of the control. Internal resistance was estimated from the slope of the plot of voltage versus current. The rapid reduction of the internal resistance can greatly enhance the output power. It was reported that adding 20% graphite flake into SMFC improved the power output 42.3% (from 0.26 mW/m^2 to 0.37 mW/m^2) [26, 27]. In our case, the control group had an internal resistance of 510 Ω and the SMFCs with rice straw pretreatment decreased the internal resistance. The internal resistance of the SMFC-H_2SO_4 and the SMFC-H_2O_2 were 430 Ω and 449 Ω. When compared to the control, the SMFC-NaOH generated the lowest internal resistance (301 Ω), thus yielding the highest $P_{max.}$

3.2. Electrode potential

In order to understand the differences, in electricity generation, between the different SMFCs, anode and cathode potentials versus an Ag/AgCl reference were determined. The cathode potentials of the SMFC-NaOH reached comparatively high values of about 200 mV within 5 days. This was faster than that which the other SMFCs reached. Carbon felt as cathode was easily form biocathodes [28] and improved the cathode potential [14]. SMFCs with NaOH pretreated release the more soluble organic matter and may stimulate the growth of microbes in the cathode region and thus accelerate the biocathode formation rates. After that, the cathodes of the all the SMFCs were almost the same through 30 days (Figure 3A). The kinetics of electron transfer from microorganisms to the anode was mainly restricted by the anode potential [24]. Compared to the SMFC-H_2O_2 (-194 mV), the other SMFCs had higher initial anode potentials (more negative) (Figure 3B). This lowest anode potential phenomenon led to the lowest voltage of the SMFC-H_2O_2, which implies that rice straw, with hydrogen peroxide, may reduce the formation of biofilms on the anode. After this initial period, the anode potential of the control fluctuated from -350 mV to -250 mV, while the anode potential of the other SMFCs fluctuated from -400 mV to -300 mV over the 30 days of operation. The results show that, to a certain extent, pretreatment of the rice straw was beneficial to the anodic oxidation reaction.

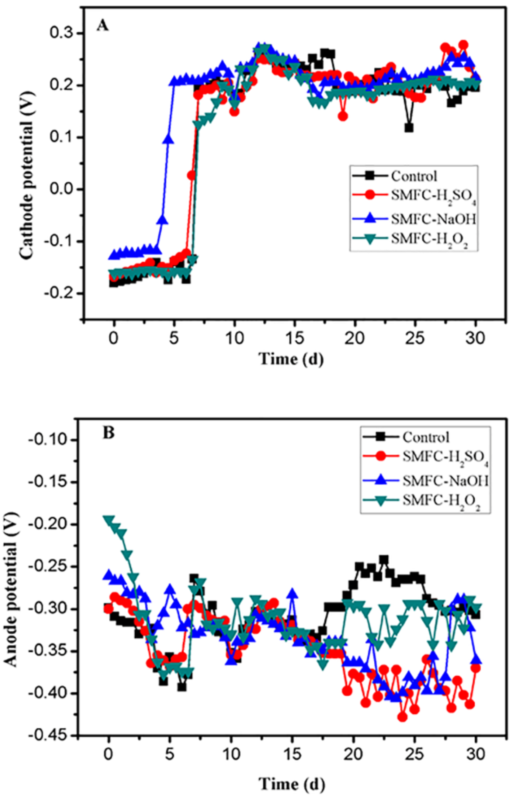

Figure 3. Working potential produced by the (A) cathodes and (B) anodes of the SMFCs with rice straw, after pretreatment with different reagents, from 0-30 days.

After 30 days, the cathode potential of all the SMFCs fluctuated from 200 mV to 300 mV (Figure 4A). When compared to the cathode potential differences, the anode potential differences were obvious. As shown in Figure 4B, the fastest increase in anode potential was produced by the control; its anode potential reached -13 mV on day 30 and became stable until the end of the experiment. This implies that the oxidation rate of the organic matter, in the control, was the slowest, followed by the SMFC-H_2O_2 and the SMFC-H_2SO_4, in which the anode potential increased to -9 mV and -4 mV by day

43, respectively. The SMFC-NaOH had the longest time for maintaining the higher anode potential (higher negative). By day 56, the anode potential of the SMFC-NaOH had increased to -6 mV. At the end of the experiment, the SMFC-NaOH still had lower (higher negative) anode potentials (-66 mV), when compared to the control (15 mV).

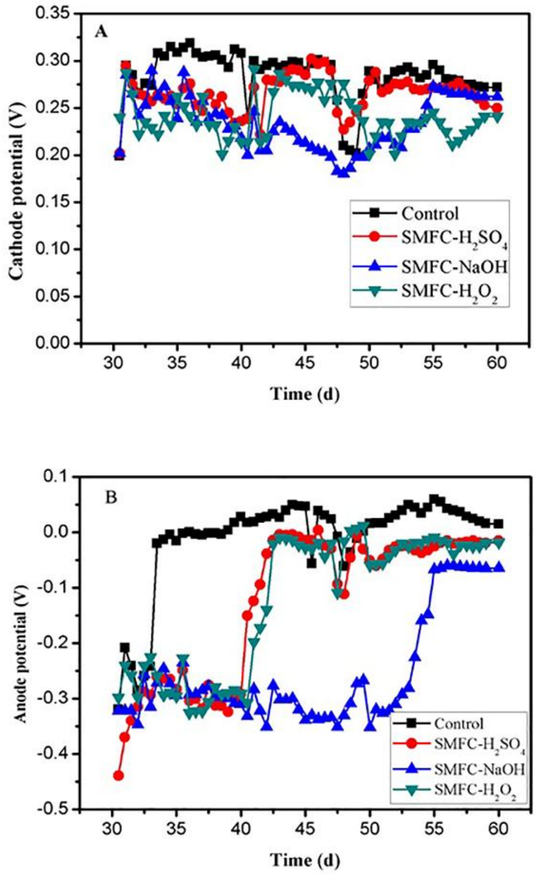

Figure 4. Working potential produced by the (A) cathodes and (B) anodes of the SMFCs with rice straw after pretreatment with different reagents, from 30-60 days.

3.3. Characteristics of rice straw after pretreatment

As shown in the SEM figure (Figure 5), the surface of untreated rice straw appears very compact with lignin sheltering hemicellulose and cellulose, and it is not possible to identify any fibers. SEM images of the rice straw with the NaOH treatment were similar to those of the rice straw with the acid treatment, but more hemicellulose and cellulose leaked from the lignin, which was consistent with the previous report [29]. Microfibers in the rice straw with the NaOH treatment were clearly visible like those from the acid treatment. The rice straw's structure was highly fibrillated by the hydrogen peroxide pretreatment, when compared to the other pretreatments. The surface of the rice straw with the hydrogen peroxide pretreatment was smooth, while the acid and alkali treatments led to a rough surface. The changes to the rice straw resulted in an increase in the porosity and the external surface area, which favors the contact of anaerobic microorganisms in the SMFC reaction [30].

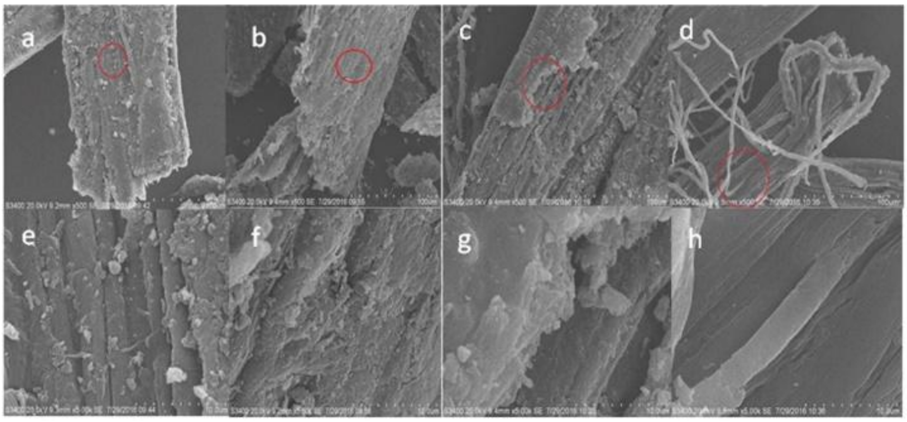

Figure 5. SEM of rice straw with no treatment(a,e), H_2SO_4 pretreatment(b,f), NaOH pretreatment(c,g), H_2O_2 pretreatment(d,h) in low and high scale, respectively.

The effect of various chemical pretreatments on the composition of rice straw has been presented in Figure 6. It was observed that the composition of rice straw had been significantly affected by the pretreatment methods. A remarkable decrease in lignin content has been demonstrated by the acid treatment (20.6%), in comparison to the untreated control (50.2%); furthermore, the lignin content decreased to 8.5% via the alkali treatment. Therefore, the cellulose content increased from 37.7% (control) to 67.4% (acid treatments) and 80.2% (alkali treatment). Hemicellulose content had a little change undergoing the acid and alkali treatments, maintained at about 12%. After the hydrogen peroxide pretreatment, lignin content was dropped to 13%, and hemicellulose content was significantly decreased to 5%, yielding a high cellulose content (80.7%).

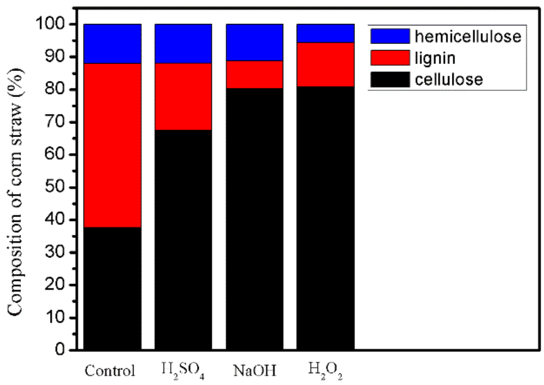

Figure 6. Compositions of corn straw pretreated with different reagents

In recent years, the development of sensors for ecosystem observation and pollution detection [31,32] required the development of reliable and scalable power supplies. SMFCs could be used as alternate power sources for these sensors, and at the same time, the SMFCs can turn the endless sources of organic matter, in the solid phase, into electricity. However, their limited output power has failed to meet the requirements for continuously running these sensors preventing their widespread use. The maximum output power of the SMFC, without other operating characteristics [33,34], was

1∼4 mW/m^2. Their maximum output power was further increased (> 100 mW/m^2) via the application of some improved methods, such as increasing the oxygen reduction rate of the cathode [35,36], improvement of sediment/soil conductivity [37,38] and improving the substrate mass transfer of the anode [4,16]. In these factors, the substrate mass transfer of the anode will also affect the longer sustained discharge time of the SMFC, which was another key parameter for power supply, in addition to the maximum output power. In a previous study [4], we proposed that biomass added into the sediment/soil inside the anodes of these SMFCs can increase their output power, but as a result, the higher lignin content, of straw, yielded a low degradation efficiency in the SMFC. In this paper, we demonstrated that the use of rice straw with pretreatment, as the substrate, can extend the sustained discharge time of an SMFC, at a higher voltage. The sustained discharge time of the SMFC-NaOH, at higher voltage, lasted almost twice as long, in comparison with the control. Although both acid and alkali pretreatments can destroy lignocellulose, the alkali pretreatment is more destructive to the structure of the lignin, releasing more cellulose (Fig.5 and 6), which is beneficial to the anodic oxidation reaction. The hydrogen peroxide pretreatment not only destroyed the structure of the lignin, but also dissolved some of the hemicellulose, resulting in a decline in the total amount of available organic matter. Furthermore, pretreatment with hydrogen peroxide can make the surface of the rice straw smooth; and the processing of the straw may not expend all of the available oxidants, leaving some of the H_2O_2 or other, possibly pretreatment byproduct oxidants, still available. This may explain why at the start, the voltage in the SMFC-H_2O_2 was lower than that of other groups and why its sustained discharge time, at higher voltage, was lower than that of the SMFC-NaOH. However, the different reagents used in the pretreatment of the straw did not significantly increase the maximum output power in the experiments, this may be due to higher organic matter (LOI content) in soil, and the low electron transfer rate, implying that more electron collectors, within the anode regions [39], may increase the power density of the SMFCs with straw.

4. CONCLUSION

In this work, the straw after pretreatment added to the SMFC reactor, can significantly improve the voltage and discharge time. It also demonstrated good reproducibility. The relevant analysis show pretreatment is the reason for the improvement of SMFC performance. Thus, showing that our pretreatment effect is significant.

ACKNOWLEDGEMENTS
Authors would like to thank Mr. Lance Nevard for English proofreading. This work was supported by CAS Key Laboratory of Bio-based Materials (No: KLBM2016009); the National Science Fund of China (Grant No.: 21390201); the Major projects of natural science research in Jiangsu Province (Grant No.: 15KJA530002); Fund from the State Key Laboratory of Materials-Oriented Chemical Engineering (ZK201605, KL15-07), the Priority Academic Program from Development of Jiangsu Higher Education Institutions.

References

1. B.E. Logan and J.M. Regan, *Trends Microbiol.*, 14 (2006) 512.
2. D.R. Bond, D.E. Holmes, L.M. Tender and D. R. Lovley, *Science*, 295 (2002) 483.
3. C.T. Wang, F.Y. Liao and K. S. Liu, *Int. J. Hydrogen Energy*, 38 (2013) 11124.
4. T.S. Song, D.B. Wang, S. Han, X.Y. Wu and C.C. Zhou, *Int. J. Hydrogen Energy,* 39 (2014) 1056.
5. X. Xu, Q.L. Zhao and M.S. Wu, *RSC Adv.*, 5 (2015) 62534.
6. C.E. Reimers, L.M. Tender, S. Fertig and W. Wang, *Environ. Sci. Technol.*, 35 (2001) 192.
7. C. Donovan, A. Dewan, D. Heo and H. Beyenal, *Environ. Sci. Technol.*, 42 (2008) 8591.
8. C. Donovan, A. Dewan, D. Heo, Z. Lewandowski and H. Beyenal, *J. Power Sources* , 233 (2013) 79.
9. Y.R.J. Thomas, M. Picot, A. Carer, O. Berder, O. Sentieys and F. Barriere, *J. Power Sources*, 241 (2013) 703.
10. X. Cao, H.L. Song, C.Y. Yu and X.N. Li, *Bioresour. Technol.*, 189 (2015) 87.
11. W.W. Li and H.Q. Yu, *Biotechnol Adv.*, 33 (2015) 1.
12. T.S. Song, Z.S. Yan, Z.W. Zhao and H.L. Jiang, *J. Chem. Technol. Biotechnol.*, 85 (2010) 1489.
13. L. Hsu, B. Chadwick, J. Kagan, R. Thacher, A. Wotawa-Bergen and K. Richter, *RSC Adv.*, 3 (2013) 15947.
14. T.S. Song and H.L. Jiang, *Bioresour Technol,* 102 (2011) 10465.
15. N. Kaku, N. Yonezawa, Y. Kodama and K. Watanabe, *Appl Microbiol Biotechnol,* 79 (2008) 43.
16. F. Rezaei, T.L. Richard, R.A. Brennan and B.E. Logan, *Environ Sci Technol,* 41 (2007) 4053.
17. T.K. Sajana, M.M. Ghangrekar and A. Mitra, *Bioresour. Technol.*, 155 (2014) 84.
18. M.J. Taherzadeh and K. Keikhosro, *Int. J. Mol. Sci.*, 9 (2008) 1621
19. G.Y.S. Mtui, *Afr. J. Biotechnol.* , 8 (2009) 1398.
20. X. Lu, Y. Zhang and I. Angelidaki, *Bioresour. Technol.*, 100 (2009) 3048.
21. M. Zheng, X. Li, L. Li, X. Yang and Y. He, *Bioresour. Technol.*, 100 (2009) 5140.
22. S.H.A. Hassan, S. M. F. G. El-Rab, M. Rahimnejad, M. Ghasemi, J. H. Joo, S. O. Yong, I. S. Kim and S.E. Oh, *Int. J. Hydrogen Energy*, 39 (2014) 9490.
23. B.E. Logan, B. Hamelers, R.A. Rozendal, U. Schrorder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete and K. Rabaey, *Environ. Sci. Technol.* , 40 (2006) 5181.
24. Y. Ziaie-Shirkolaee, J. Mohammadi-Rovshandeh, P. Rezayati-Charani and M.B. Khajeheian, *Bioresour. Technol.*, 99 (2008) 3568.
25. J. Zhao, X.F. Li, Y.P. Ren, X.H. Wang and C. Jian, *J. Chem. Technol. Biotechnol.*, 87 (2012) 1567.
26. A. Dominguez-Garay, A. Berna, I. Ortiz-Bernad and A. Esteve-Nunez, *Environ. Sci. Technol.* , 47 (2013) 2117.
27. S.L. De, P. Boeckx and W. Verstraete, *Appl. Microbiol. Biotechnol.*, 87 (2010) 1675
28. M. Lenin Babu and S. Venkata Mohan, *Bioresour Technol*, 110 (2012) 206.
29. Z.H. Hu and Z.Y. Wen, *Biochem. Eng. J.* , 38 (2008) 369.
30. X. Liu, S. M. Zicari, G. Liu, Y. Li and R. Zhang, *Bioresour. Technol.*, 185 (2015) 150.
31. I.F. Akyildiz, D. Pompili and T. Melodia, *Ad. Hoc. Netw.*, (2005) 257.
32. E. Santi, S. Paloscia, S. Pettinato and G. Fontanelli, *Int. J. Appl. Earth.*, 48 (2016) 61.
33. S.W. Hong, I.S. Chang, Y.S. Choi, B.H. Kim and T.H. Chung, *Bioprocess Biosyst. Eng.*, 32 (2009) 389.
34. G. Martins, L. Peixoto, D.C. Ribeiro, P. Parpot, A.G. Brito and R. Nogueira, *Bioelectrochemistry*, 78 (2010) 67.
35. Z. He, H.B. Shao and L.T. Angenent, *J. Biosens. Bioelectron.*, 22 (2007). 3252.
36. D.B. Wang, T.S. Song, T Guo, Q.L. Zeng and J.J. Xie, *Int. J. Hydrogen Energy*, 39 (2014) 13224.

37. B.M. Lenin and M.S, Venkata. *Bioresour. Technol.*, 110 (2012) 206.
38. A. Domı´nguez-Garay, A. Berna, I. Ortiz-Bernad and A. EsteveNu´nez, *Environ. Sci. Technol.*, 47 (2013) 2117.
39. B.C. Liu, I. Williams, Y. Li, L. Wang, A. Bagtzoglou, J. Mccutcheon and B. Li, *J. Biosens. Bioelectron.*, 79 (2016) 435.