Nanomodification of the electrodes in microbial fuel cell: Impact of nanoparticle density on electricity production and microbial community

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Highlights

- Improved power generation of MFC with Au nanoparticles modified carbon paper.
- Coulombic efficiency increased with Au nanoparticle density.
- Different Au nanoparticles densities resulted in different microbial communities.
- More diverse bacterial communities with higher Au nanoparticle densities.

Abstract

The nano-decoration of electrode with nanoparticles is one effective way to enhance power output of microbial fuel cells (MFCs). However, the amount of nanoparticles used for decoration has not been optimized yet, and how it affects the microbial community is still unknown. In this study, different densities of gold (Au) nanoparticles were sputtered on carbon paper as electrodes of MFCs. The results show that power generation increased with Au nanoparticle density on the electrodes. The highest power density was obtained by depositing carbon paper with an Au thickness of 50 nm and 100 nm on each side, respectively, which was 1.22–1.88 times higher than that obtained with plain carbon paper electrode (control). Furthermore, the Coulombic efficiency was increased with the Au density. Consequently, the maximum lag time before stable power generation was shortened by 1.22 times the lag time of the control. Different densities of Au nanoparticles also resulted in different microbial communities on the anode. More diverse bacterial communities were found with higher Au nanoparticle densities. These results provide new dimensions in understanding electrode modification with nanoparticles in MFC systems.

Article history:
Received 3 July 2013
Received in revised form 6 November 2013
Accepted 23 November 2013
Available online 20 December 2013

Keywords:
Microbial fuel cell
Nanoparticles
Electricity generation
Electrodes modification
Microbial community

1. Introduction

The use of fossil fuels in the recent years has accelerated a global energy crisis. The release of CO₂ from the combustion of fossil fuels causes global climate changes. Therefore, a carbon-neutral, sustainable energy sources as alternatives to fossil fuels is needed to alleviate the global energy crisis and climate change. Bioelectrochemical systems (BESs) provide an innovative and very promising technology for renewable energy generation and wastewater treatment. Moreover, BESs is a rapidly emerging technology with several application possibilities such as electricity production, seawater desalination, biosensor, microbial electrosynthesis and bioremediation [1–4]. Microbial fuel cells (MFCs) as a typical BES in which microorganisms mediate the direct conversion of chemical energy stored in organic matter or bulk biomass into electrical energy has gained considerable interests among academic researchers in recent years. In a typical MFC an ion-exchange membrane separates the anode and the cathode chambers. In the anode chamber bacteria grow in a solution by oxidizing organic matter and releasing hereby protons and electrons that react in the cathode chamber by creating water. Electricity is generated when the electrons travel between the chambers through an external circuit [5–7].

Over the last decade the power density of MFCs has increased with 10,000 orders of magnitude [8,9]. Even with the remarkable improvements in electricity generation, more effort is still required to promote field applications of MFCs. A key limitation in energy production from MFC is the electrode material design. Bacterial adhesion, electron transfer and substrate oxidation are all factors that are directly dependent on the electrode performance [9–12]. To overcome the hurdles of low electricity generation caused by the electrode material, the electrode can be modified with nanoparticles that decrease the transfer resistance for electrons.
Nanostructured electrodes have been proven to play an important role in the improvement of power output in MFCs [13,14]. Nanomodified electrodes can contribute in improving the bacteria attachment due to the lower transfer resistance for electrons than in conventional electrodes [13]. A wide range of electrode designs have been developed in previous studies in order to improve MFC performance [14–16]. Sharma et al. decorated carbon paper electrodes with platinum (Pt) resulting in a 6-fold increase in power density [17]. Sun et al. coated carbon paper electrodes with carbon nanotubes achieving a 20% increase in power density compared to plain carbon paper [18]. Another work showed that plain graphite electrodes decorated with gold (Au) nanoparticles resulted in a 20-fold higher current density, while Pd-decorated electrodes produced 50–150% higher electricity output than graphite [19]. A maximum power density of 228 mW m⁻² was observed when using polytropo coated carbon nanotubes on carbon paper [20], while iron oxide coated carbon paper presented a 2.75-fold increase in power density [21]. Moreover, Xu et al. modified graphite disks with Fe nanoparticles hereby achieved a 5.89-fold higher current density generation than plain graphite electrodes [22]. An attempt to enhance the current output done by Alatraktchi et al. showed that Titanium (Ti) and Au coated nanograss structured Si electrodes resulted in a 63 times higher power generation than Ti and Au coated on plain Si electrodes [23]. The study also concluded that the power production in MFC using carbon paper modified with Au nanoparticles was enhanced with 250% only by coating on one side [23]. Au is known to be unreactive, however, nanoscale Au particles completely change the Au properties, hereby making them catalytically active [24]. Though it has been proven from above mentioned works that Au nanoparticles can enhance the power generation, the relationship between the amount/density of Au nanoparticles applied on the electrode and power generation has never been explored systematically. In addition, how different densities of nanoparticles influence the microbial community of the biofilm formed in the anode is still unclear. Furthermore, it should be noted that the amount/density of nanoparticles used for decoration is also critical for scaling up of MFCs in different applications.

Since a lot of MFC electrode modification have been done using nanotechnology, it is therefore of great importance to investigate how the nanoparticle amount affects the electricity production and the microbial community.

In the current study the performance of an MFC using carbon paper electrodes modified with Au nanoparticles was investigated. The relationship between the density of Au particles on carbon paper and the electricity production was elucidated. Moreover, the microbial community established as biofilm on the decorated electrodes was examined.

2. Material and methods

2.1. Electrode fabrication

Five different sets of carbon-paper-based electrodes were nano-modified, i.e. sputtered with Au nanoparticles, along with a set of control electrodes, with a size of 3 x 3 cm each. Physical vapour deposition (PVD) was used to coat the electrode surfaces [25]. Carbon paper (Toray carbon paper, E-TEK, USA) electrode sets were deposited with Au nanoparticles using sputter deposition with HUMMER-machine (Anatech Hummer 6.2, USA) for 5 (named as E5), 10 (E10), 15 (E15) and 25 (E25) min for each set of electrodes, respectively, in a pressure of 100 mTorr and a discharge current of 10 mA. The electrodes were deposited with Au nanoparticles with the same sputter time on both sides. A sketch of the Au nanoparticles on carbon paper can be seen in Fig. 1a.

A set of carbon paper electrodes was coated with a layer of 50 and 100 nm Au on each side, respectively (E50+100), using an electron beam physical vapor deposition (EBPVD) machine (Alcatel SCM600 e-beam and sputter tool, Germany). A sketch can be seen in Fig. 1b. The nanofabricated electrodes are gathered and presented in Table 1.

![Fig. 1. Schematic representation of nanofabricated electrodes. (a) Carbon paper sputtered with gold nanoparticles. (b) Carbon paper deposited with a nanolayer of gold (reconstructed from Alatraktchi et al., 2012). (c) Line scan of 2 nanoparticles imaged by Scanning Electron Microscopy (right). Intensity profile of line scan (left). The diameters of the particles can be measured by the width of the peaks (red lines). The distance between the particles is the distance between the centrum of the peaks (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
The morphology of the electrodes was visualized before operation using Scanning Electron Microscopy (SEM Zeiss). After operation the electrodes were characterized again using another SEM (JEOL JSM 5500LV Scanning Electron Microscope) in order to observe any changes of the nanostructures due to the process. The density of the Au nanoparticles has been estimated for all the electrodes using the imaging processing program ImageJ (Version 1.45s, NIH, USA). Line scans with a length of 2000 nm were taken and profile plots were drawn. All line scans were taken along carbon fibers in order to maintain the same height. The data were processed by subtracting the background of each image from the profile data series. It was assumed that the mean value of 10 measurements of the background was the background intensity that was subtracted from the signals. Moreover, the sizes of the Au nanoparticles were measured in order to emphasize the impact of the size of the particles on the electricity production.

### 2.4. Microbial community analysis

The anode electrodes at the end of operation were washed with sterile distilled water to remove any attached debris, a sterilized scalpel was hereafter used to scrape the attached biofilm. Qiaamp DNA Stool Mini Kit (Qiagen catalog no. 51504) was used according to the instructions of the manufacturer to extract the DNA that was first amplified using the universal primers 27F (5-AGA GTT TGA TCM TGG CTC AG-3) and 1492r (5-TAC GGY TACTT TTA CCA CTT-3). Subsequently the products were amplified again with the primer set 357F, containing a GC clamp (5-CCG CCG CCG CGC GCC GCCGGG GCC GGG GCA CGG GCC TAC GGC AGG CAG CAG-3), and 518r (5-ATT ACC GCG GGT CCTGG-3). The PCR amplifications were accomplished with a thermocycler (Eppendorf) as described by Muyzer et al. [27]. Polyacrylamide gels, 6% (wt/vol), with a denaturant gradient between 40% and 60% were used to separate the PCR products (25 μl). The Dcode Universal Mutation Detection System (Bio-Rad) was used for denaturant gradient gel electrophoresis (DGGE). It was operated in 0.5*Tris–acetate–EDTA buffer at 120 V for 30 min and subsequently at 60 V for 14 h (60 °C), and then the gels were stained using SYBR gold (Bio-Medinc) for 40 min and destained in 0.5*Tris–acetate–EDTA buffer (pH 8.0). Afterwards the DNA bands were observed with a GelDoc image analyzer (Bio-Rad Laboratories). Lanes from DGGE were analyzed with Quantity One Software (Bio-Rad Laboratories). Bands were chosen, cut, excised from the gel and sent for sequencing (Macrogen, Netherlands), where the sequences were exposed to Basic Local Alignment Search Tool (BLAST) and Ribosomal Database Project analysis. Ribosomal Database Project’s classifier and Seqmatch determined phylogeny. The sequenced 16S rRNA data were subsequently submitted to GenBank (Bethesda, Maryland, USA), where the nucleotide sequence accession numbers JX230978–JX230993 were given.

### 3. Results and discussion

#### 3.1. Au nanoparticle density impact on electricity generation

An example of a line scan measurement is seen in Fig. 1c. The diameter is observed in the top of the intensity peak (red lines), where the shadowing intensity is minimized, hereby achieving the right diameter without extensions. Janssens et al., have shown that Au nanoparticles less than 10 nm in diameter begin to show catalytic activity, [24] where the Au nanoparticles are capable of decreasing the anodic resistance. Line scans of the Au nanoparticles widths showed diameters less than 5 nm and up to 20 nm. There are possibly even smaller nanoparticles that were undetected due to the limited microscope resolution. This means that the Au nanoparticles that were sputtered on the electrodes had optimal sizes for catalyzing the electricity generation in accordance with the catalytic limit of 10 nm.

The centrum from peak to peak in Fig. 1c is the distance between the nanoparticles. Different sputter times resulted as expected in different Au nanoparticle densities as seen in Fig. 2. Here each peak corresponds to an Au nanoparticle. The line scan was done arbitrarily and therefore it did not necessarily get through the diameters, thus the peak widths do not correspond to the widths of the nanoparticles. Fig. 2a shows 22 nanoparticles in a 2000 nm scan of E5, the corresponding SEM-pictures clearly show the nanoparticles (Fig. S1a and b, Supplementary data). E10 had about 35 peaks in the same interval (Fig. 2b and Fig. S1c and d), while E15 had even denser nanoparticles per 2000 nm (Fig. 2c and Fig. S1e and f). For E25 a thin deposition layer was observed instead of independent nanoparticles (Fig. S1g and h). E50–100 had a thicker layer than the previous electrodes (Fig. S1i and j).

Stable power generation was obtained with all the fabricated electrodes after two consecutive batches operation. An example of one cycle of stable power generation is shown in Fig. 3. The maximum power density of the control MFC was 306.2 mW m$^{-2}$ while the other MFCs with the electrodes E5, E10, E15 and E25, had a steep increase in maximum power density increasing in the same

#### 2.2. MFC setup and calculations

The five nanofabricated electrode sets were tested in conventional H-chamber MFCs along with a control test of conventional carbon paper. Two 300 ml bottles (250 ml liquid volume each) were connected by a tube separating the anode and cathode by a proton exchange membrane. Insulated copper wires connected the electrodes according to previous studies [23,26]. All the anode chambers were filled with domestic wastewater collected from primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark). The wastewater was modified with acetate to reach the final COD concentration of 1000 ± 60 mg L$^{-1}$.

The cathode chambers were filled with 50 mM ferricyanide buffer at 120 V for 30 min and subsequently at 60 V for 14 h (60 °C), and then the gels were stained using SYBR gold (Bio-Medic) for 40 min and destained in 0.5*Tris–acetate–EDTA buffer (pH 8.0). Afterwards the DNA bands were observed with a GelDoc image analyzer (Bio-Rad Laboratories). Bands were chosen, cut, excised from the gel and sent for sequencing (Macrogen, Netherlands), where the sequences were exposed to Basic Local Alignment Search Tool (BLAST) and Ribosomal Database Project analysis. Ribosomal Database Project’s classifier and Seqmatch determined phylogeny. The sequenced 16S rRNA data were subsequently submitted to GenBank (Bethesda, Maryland, USA), where the nucleotide sequence accession numbers JX230978–JX230993 were given.

### Table 1

<table>
<thead>
<tr>
<th>Deposition type</th>
<th>Au deposition on carbon paper</th>
<th>Max. power density (mW m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter deposition</td>
<td>0 min (control)</td>
<td>306.2</td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>327.0</td>
</tr>
<tr>
<td></td>
<td>10 min</td>
<td>339.2</td>
</tr>
<tr>
<td></td>
<td>15 min</td>
<td>355.1</td>
</tr>
<tr>
<td></td>
<td>25 min</td>
<td>363.4</td>
</tr>
<tr>
<td>Electron-beam deposition</td>
<td>50 + 100 nm</td>
<td>374.9</td>
</tr>
</tbody>
</table>

The five nanofabricated electrode sets were tested in conventional H-chamber MFCs along with a control test of conventional carbon paper. Two 300 ml bottles (250 ml liquid volume each) were connected by a tube separating the anode and cathode by a proton exchange membrane. Insulated copper wires connected the electrodes according to previous studies [23,26]. All the anode chambers were filled with domestic wastewater collected from primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark). The wastewater was modified with acetate to reach the final COD concentration of 1000 ± 60 mg L$^{-1}$.

The cathode chambers were filled with 50 mM ferricyanide buffer at 120 V for 30 min and subsequently at 60 V for 14 h (60 °C), and then the gels were stained using SYBR gold (Bio-Medic) for 40 min and destained in 0.5*Tris–acetate–EDTA buffer (pH 8.0). Afterwards the DNA bands were observed with a GelDoc image analyzer (Bio-Rad Laboratories). Bands were chosen, cut, excised from the gel and sent for sequencing (Macrogen, Netherlands), where the sequences were exposed to Basic Local Alignment Search Tool (BLAST) and Ribosomal Database Project analysis. Ribosomal Database Project’s classifier and Seqmatch determined phylogeny. The sequenced 16S rRNA data were subsequently submitted to GenBank (Bethesda, Maryland, USA), where the nucleotide sequence accession numbers JX230978–JX230993 were given.
The highest maximum power density of 374.9 mW m$^{-2}$ was achieved by E$_{50+100}$. This is an increase in electricity generation with 22%. The decrease of power generation at end of batch operation is due to the depletion of substrate [28].

The stable power generation in the control MFC operation lasted for about 370 h (Fig. 3). There was an increasingly longer stable time proportional with the Au density on the carbon paper electrodes. The longest stable time of about 450 h was observed in the MFC operated with E$_{50+100}$. This is an increase from the stable time of the control with about 80 h equaling an enhancement of 22%.

The maximal power production obtained with different external resistances can be seen in Fig. 4, which shows almost perfect hyperbolic power density functions. It is seen that the internal resistance gets lower as the Au density on the electrode gets higher. The highest maximum power density observed was 461.6 mW m$^{-2}$ obtained at 1180.6 mA/m$^2$ current density (368 $\Omega$) for E$_{50+100}$. This is an enhancement of the control result (without Au nanoparticles, 361.5 mW m$^{-2}$) with 28%.

3.2. Change in COD content

The change in COD content was measured during the experiment (Fig. 5). It is observed that the COD content for the control MFC was decreasing most rapidly compared to the other nanomodified electrodes. While the COD content was completely removed after 185 h, the MFCs operated with E$_5$ and E$_{10}$ had a removal time of 270 h. The last three electrodes E$_{15}$, E$_{25}$ and E$_{50+100}$ all took 285 h for complete COD removal. It is clearly seen from Fig. 5 that less presence of Au nanoparticles results in shorter time for depletion of the COD. Even though the levels where the COD content was completely removed were close to each other for some MFCs, it was still the high Au nanoparticle density decorations that gave the longest removal time. Even the COD degradation was faster in the control reactor, the CE increased with Au density from 11.3% (control) to 15.4% (E$_{50+100}$).

It is indeed peculiar that power density increased in the reactor with the nano-modification electrode, while the removal of COD was lower compared to the control MFC. One explanation could be that different bacteria were enriched in these reactors. For example, the microbial community enriched in the control reactor could be dominated by non-electrochemically active bacteria, such as aerobic bacteria, as a result of oxygen diffusion from the cathode.
chamber. It has been reported that the COD removal with aerobic bacteria is much faster than that with electrochemically active bacteria [29]. It was indeed found that different microbial community compositions were enriched on the electrodes with different nano densities. It is yet not known which bacteria have electrochemical activity. Therefore it was not possible to determine the composition of electrochemically active bacteria (EAB) in these reactors. Beside aerobic bacteria, methanogens and denitrifiers could also consume COD, but as no methane, nitrogen, nitrate or nitrite production were detected at the end of the test, the analysis of anaerobic activity was unnecessary. Furthermore, there is no evidence that the CE is directly proportional to the COD removal. It is possible that the EAB removed the COD slower than aerobic bacteria or others, but converted most of the removed COD to electricity. Moreover, according to the calculation of CE, CE is directly proportional to electron production while it is inversely proportional to the COD removal. According to the definition for CE, CE indicates the ratio of the electrons stored in the COD that are converted to electricity but not the COD removal, which could explain the higher CE but lower COD removal with nano-modified electrodes compared to the control.

3.3. Microbial community analysis

The biofilm samples were taken from the anodes at the end of first and third batch operation. DGGE profiles of the different operated MFCs showed notably different community compositions. Based on the 16S rDNA gene library results (Table 2, Fig. 6), the control electrode in the last batch was colonized by *Gammaproteobacteria* (25% of sequences). The electrode E5 was dominated by *Sphingobacteria* (12.5%), while the electrode E10 was dominated by *Negativicutes* (6.3%). Biofilm analysed from E15 was composed of *Gammaproteobacteria* (25%), *Bacteroidia* (18.8%) and *Deltaproteobacteria* (6.3%). The electrode E25 was colonized by *Sphingobacteria* (12.5%), *Flavobacteria* (6.3%) and *Clostridia* (12.5%). *Bacteroidia* (18.8%), *Betaproteobacteria* (12.5%), *Gammaproteobacteria* (25%) and *Clostridia* (12.5%) were detected in the biofilm on E50-100.

The microbial communities in the samples taken from the last batch were more diverse than that taken from the first batch. This is due to a thicker biofilm layer obtained in the last batch, while the biofilm was still being created during the first batch hereby giving different microbial community compositions.

Earlier studies have observed that *Gammaproteobacteria* and *Bacteroidetes* occurred at high numbers within libraries from electrode biofilm, in which particularly the *Gammaproteobacteria* were believed to be responsible for the electron transfer and consequently the power generation [26,30]. These two bacteria types were present in the biofilm of the control and in E15, E25, E50-100. Moreover, *Shewanella* were that were previously reported to transfer electrons to the electrodes were detected in the biofilm of E50-100 (band 16) [31].

*Deltaproteobacteria* is also believed to be responsible for the electron transfer to the electrode [32] and were detected in the biofilm of E15 with 6.3% dominance, which is a little lower than the value reported in the literature of 10% and 70%, respectively [26,33]. *Flavobacteria* and *Bacteroidia* are earlier identified as dominant bacteria for electricity production [4,26,34]. Moreover, *Clostridia* have also shown electrochemical activity in previous studies [35].

The microbial community composition observed in this study shows that the biofilm of the different electrodes was dominated by exoelectrogenic bacteria. However, two observed bacteria types that were present in the biofilm have unknown exoelectrogenic activity, namely *Negativicutes* and *Sphingobacteria*. Nevertheless, since higher electricity was generated using both E5 and E10 and they were only cultured with the above mentioned bacteria; it indicates that they were also exoelectrogenic microbes. The variety of the bacterial colonies on the electrodes might be due to different catalytic activity of the electrode structures caused by varying Au nanoparticle densities.

![Fig. 5. Effect of the nanofabricated electrodes on organic removal.](image)

### Table 2

<table>
<thead>
<tr>
<th>Band</th>
<th>GenBank Accession No.</th>
<th>Closest relatives (% sequence similarity</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>JX230978</td>
<td>Uncultured Acidaminococcus sp. L8–D2 (86%)</td>
<td>Negativicutes</td>
</tr>
<tr>
<td>2</td>
<td>JX230979</td>
<td>Bacterium enrichmen culture clone 005/2012 (96%)</td>
<td>Bacteroidia</td>
</tr>
<tr>
<td>3</td>
<td>JX230980</td>
<td>Uncultured Shewanella sp. J6 (91%)</td>
<td>Sphingobacteria</td>
</tr>
<tr>
<td>4</td>
<td>JX230981</td>
<td>Uncultured Bacteroides bacterium clone L2K19UD (87%)</td>
<td>Bacteroidia</td>
</tr>
<tr>
<td>5</td>
<td>JX230982</td>
<td>Uncultured Flavobacterium sp. clone 42 (95%)</td>
<td>Flavobacteria</td>
</tr>
<tr>
<td>6</td>
<td>JX230983</td>
<td>Uncultured Ferribacterium sp. Depth_24 to 36–20 (87%)</td>
<td>Betaproteobacteria</td>
</tr>
<tr>
<td>7</td>
<td>JX230984</td>
<td>Uncultured bacterium clone N2_4_2043 (92%)</td>
<td>Clostridia</td>
</tr>
<tr>
<td>8</td>
<td>JX230985</td>
<td>Uncultured bacterium clone MAR2_504 (92%)</td>
<td>Bacteroidia</td>
</tr>
<tr>
<td>9</td>
<td>JX230986</td>
<td>Uncultured bacterium clone B-57 (91%)</td>
<td>Gammaproteobacteria</td>
</tr>
<tr>
<td>10</td>
<td>JX230987</td>
<td>Uncultured bacterium clone FR0701_2aa4bd05 (94%)</td>
<td>Gammaproteobacteria</td>
</tr>
<tr>
<td>11</td>
<td>JX230988</td>
<td>Iron-reducing bacterium enrichmen culture clone HN117 (98%)</td>
<td>Clostridia</td>
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<tr>
<td>12</td>
<td>JX230989</td>
<td>Uncultured bacterium clone ZWBS-2 (96%)</td>
<td>Gammaproteobacteria</td>
</tr>
<tr>
<td>13</td>
<td>JX230990</td>
<td>Uncultured Sorangium sp. clone Plot21-H07 (91%)</td>
<td>Deltaproteobacteria</td>
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<tr>
<td>14</td>
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<td>Sphingobacterium sp. HPC429 (91%)</td>
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<td>15</td>
<td>JX230992</td>
<td>Uncultured bacterium clone 4783938 (96%)</td>
<td>Betaproteobacteria</td>
</tr>
<tr>
<td>16</td>
<td>JX230993</td>
<td>Shewanella oneidensis strain SP-22 (93%)</td>
<td>Gammaproteobacteria</td>
</tr>
</tbody>
</table>

- a Corresponding to the number shown in the DGGE profile.
- b Nucleotide sequences have been deposited in the Genbank database.
- c The phylotypes were assigned to phyla based on Ribosomal Database Project II (RDP II) taxonomy classifications.
- d Percent values represent similarities between the associated DGGE band sequence and the closest match sequence from GenBank.
interesting research area would be to examine if Au nanodecora-
tions attract certain bacterial communities. The biocompatibility of
Au nanoparticles should also be considered in future research,
since decomposition of the nanoparticles might occur. However,
early studies have shown that Au nanoparticles do not show
any indication of toxicity [36]. The biocompatibility and decom-
position of other nanoparticles such as carbon in MFC or other BESs
could also be one of important research directions in the future.

The applied technology to modify the electrodes does not only
contribute to high electricity production in MFC, but it can also
be used to enhance the energy production and energy saving in
several other bioelectrochemical systems such as electrolysis cells
for hydrogen production, and bioelectrosynthesis of various
products.

4. Conclusion

This study is the first attempt at demonstrating the relation be-
tween the density of nanoparticles and the power production in
MFCs, in addition to studying the microbial communities observed
on different anode-types. The maximum power density of carbon
paper electrodes was improved 188% by depositing carbon paper
electrodes with Au. The stable time with maximum power produc-
tion was enhanced 122%. Furthermore, high Au nanoparticle densi-
ties on carbon paper electrodes increased Coulombic efficiency.
DNA sequencing of the biofilms extracted from the electrodes
showed exoelectrogenic microbial communities with more bacte-
rial groups on the anodes with high Au nanoparticle density.

Acknowledgements

Special thanks to Danchip DTU, Center of Nanoscopy (CEN) and
Jørn Bendslev Hansen for their support during nanofabrication and
characterization of the nanoelectrodes.

Appendix A. Supplementary material

Supplementary material associated with this article can be
found, in the online version, at http://dx.doi.org/10.1016/
j.apenergy.2013.11.058.

References

[3] Rabaye K, Rozendal RA. Microbial electrocystosis – revisiting the electrical
microbial activity and BOD in groundwater: focusing on impact of anodic
[9] Li P, Wang H, Xia X, Huang X. Carbon nanotube powders as electrode
modifier to enhance the activity of anodic biofilm in microbial fuel cells. Biosens Bioelectron
and CoMPP) and polymer binders (Nafion and PTFE) in single chamber
MnO2/carbon nanotube and polymethylphenyl siloxane as low-cost and high-

Fig. 6. Anode bacterial community profiles revealed by DGGE. W, wastewater is the
inoculum; A–F is referring to the first batch, where A is the control; G is the last batch,
and F, 50 + 100 nm Au deposition. – refers to the last batch, where C is the control; H, 5 min;
I, 10 min; J, 15 min; K, 25 min and L, 50 + 100 nm.


