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1 Surface Area Expansion of Electrodes with Grass-like Nanostructures to Enhance Electricity
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4 Generation in Microbial Fuel Cells
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Abstract

Microbial fuel cells (MFCs) have applications possibilities for wastewater treatment, biotransformation, and biosensor, but the development of highly efficient electrode materials is critical for enhancing the power generation. Two types of electrodes modified with nanoparticles or grass-like nanostructure (termed nanoglass) were used. A two-chamber MFC with plain silicium electrodes achieved a maximum power density of 0.002 mW/m^2 , while an electrode with nanoglass of titanium and gold deposited on one side gave a maximum power density of 2.5 mW/m^2 . Deposition of titanium and gold on both sides of plain silicium showed a maximum power density of 86.0 mW/m^2 . Further expanding the surface area of carbon paper electrodes with gold nanoparticles resulted in a maximum stable power density of 346.9 mW/m^2 which is 2.9 times higher than that achieved with conventional carbon paper. These results show that fabrication of electrodes with nanoglass could be an efficient way to increase the power generation.

Keywords: Microbial Fuel Cell; Deep Reactive Ion Etching; Nanoglass; Electron-Beam Evaporation; Sputter Deposition; Electricity generation

1. Introduction

Microbial fuel cells (MFCs) are bioelectrochemical devices in which microorganisms mediate the direct conversion of chemical energy stored in organic matters into electrical energy (Aelterman et al., 2006; Katuri and Scott, 2011; Logan et al., 2006; Logan, 2008; Min et al., 2005; Min and Angelidaki, 2008; Rabaey et al., 2005; Viridis et al., 2010; Wang et al., 2010; Zhang et al., 2010). Such systems have also been proven interesting for hydrogen production, seawater desalination, biosensor, and microbial electrosynthesis (Cao et al., 2009; Cheng and Logan, 2007; Rabaey, 2010; Zhang and Angelidaki, 2011).

Though promising, MFCs technology has not moved from bench scale operation due to several limitations. A main constraint of the MFC technology is the low power generation (Cheng et al., 2006a; Logan, 2008). The main challenge is therefore, to enhance electricity production, and thereby improve the possibilities for practical applications. The electrode material is a key factor for increasing MFC efficiency (Oh et al., 2004) as it affects electron transfer, bacterial attachment and substrate oxidation (Cheng et al., 2006b; Viridis et al., 2008). Carbon-paper is the most applied electrode material in an MFC due to its chemical stability, high conductivity and low price (Tsai et al., 2009). If the surface area of electrodes is increased, more space for bacteria immobilization and more electrons transfer could be possible. Furthermore, enhancing the conductivity of electrode would result in increasing electricity generation in MFC.

Because of large surface areas, short charge diffusion lengths and high diffusion rates along their grain boundaries, electrode materials with nanostructures have gained attention for improving the performance of MFCs (Yang et al., 2012). The nanostructures play an important role in extending the lifetime of electrodes and whole cells. They could also increase the microbial loading and subsequently improve the power density of MFCs. Besides, mass transfer limitation of substrates could also be relieved with nanostructures compared to conventional macro-scale structures (Yang

1 et al., 2012). Thus, fabrication of electrodes by using nanotechnology can provide new dimensions
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3 in MFC science (Higgins et al., 2011; Liang et al., 2010; Sharma et al., 2008). Previous studies have
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5 reported results with electrodes coated with nanoparticles. Fan et al. (2010) found that an anode
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7 decorated with Au nanoparticles produced current densities up to 20 times higher than plain
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9 graphite anodes in the presence of *Shewanella oneidensis* MR-1, while Pd-decorated anodes with
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11 similar morphologies produced 50-150% higher current density than graphite anodes. Yuan et al.
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13 (2011) developed a fast and convenient bacterial immobilization method by entrapping in a carbon
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15 nanoparticle matrix to improve the anode efficiency of an MFC and achieved a maximum power
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17 density of 1947 mW/m² which was much higher than that obtained with a biofilm-based carbon
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19 cloth anode (1479 mW/m²). In addition to nanoparticles (conventionally called 0D structures), 1D
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21 nanostructures such as nanotubes have also been employed for improving the power generation of
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23 MFCs. A maximum power density of 65 mW/m² was observed in an MFC with carbon-cloth
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25 electrodes coated with carbon nanotubes (Tsai et al., 2009). Compared with 0D and 1D
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27 nanostructures, 3D structures offer benefits for bioelectrode fabrication (Yang et al., 2012). 3D
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29 structures would include the best features of the 0D, 1D and 2D structures; however, electrodes
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31 with 3D nanostructures such as grass-like nanostructure (so-called nanograss) have not yet been
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33 tested in MFCs.
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42 In the current study, the properties of electrodes were improved by using different
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44 nanotechnological methods in combination with different electrode materials, in order to increase
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46 the electricity generation in an MFC. The nanostructured electrodes were made by making different
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48 so-called nanograss topographies on silicium (Si) wafers (Shieh, 2011). In addition to nanograss,
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50 well-conductive particles such as titanium (Ti), copper (Cu) and gold (Au) deposited on the
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52 nanostructured electrode samples were tested for enhancing electricity generation. Lastly, Au
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nanoparticles were sputtered onto carbon-paper electrodes. The relationships between the nanofabricated electrodes and power densities were investigated.

2. Material and methods

2.1 Electrode fabrication

All nanofabrications were done in a cleanroom. Nanograss was made by using a PEGASUS apparatus (DRIE Pegasus, Surface Technology systems, UK), usually used for etching silicon. It uses a deep reactive ion etching (DRIE) process, creating black silicon nanograss by chemical and physical interactions (Jansen et al., 1995). Nanograss topography achieves a large surface area. The PEGASUS apparatus forms plasma by ionizing SF₆ and O₂ in an electromagnetic field (Madou, 1998). The following process conditions were used as initial determinates to obtain large topography areas of the nanostructures: SF₆ flow ratio of 50, O₂ flow ratio of 50, coil power of 2800 W, platen power of 16 W and pressure of 38 mTorr. The process time for fabrication of the nanograss was 10 min. The temperature used during the etching was -10°C. Nanograss was made on four wafers. One of them, HighSi, on a Si-wafer with a resistivity of 100 Ωm and the remaining three Si-wafers (LowSi) with resistivities of 0.025 Ωm.

2.2 Deposition of electrodes

Au nanoparticles were deposited on carbon paper (Toray carbon paper, E-TEK, USA) using sputter deposition with a HUMMER apparatus (Anatech Hummer 6.2, USA) for 10 min at a pressure of 100 mTorr and a discharge current of 10 mA (Alcock, 2001). Au nanoparticles were only deposited on one side of the 3×3 cm carbon-electrodes. Carbon paper without any nano-manipulation was used as control. Electron beam physical vapour deposition (EBPVD) was used to coat the Si-wafers (Madou, 1998). An Alcatel apparatus (Alcatel SCM600 e-beam and sputter tool, Germany) was used to deposit the wafers at a vacuum pressure of 1 x 10⁻² mbar. A LowSi wafer was coated with a 100-nm layer of Cu, and another LowSi wafer was coated with 10 nm Ti and then 100 nm Au. Ti

1 was used to bind the gold tightly to the electrode. A plain LowSi wafer without nanograss was also
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3 coated with 10 nm Ti and 100 nm Au on one side, while another similar wafer was deposited with
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5 the same materials and amounts but on both sides. Another plain LowSi wafer without nanograss
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7 was coated with 100 nm Cu and the last wafer was coated with 10 nm Ti and 100 nm Cu on both
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9 sides (Table 1).
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12 2.3 Cutting of electrodes

13 The wafers were cut with a SAW dicing machine (Disco Dicing Saw, Disco Europe) to a size of
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15 3x3 cm.
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18 2.4 MFC setup

19 Electrodes were tested in an H-chamber MFC consisting of two bottles with volumes of 300 ml
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21 (250 ml liquid volume) each, connected by a tube which separates the cathode from the anode by a
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23 proton exchange membrane (Zhang et al., 2009). The different electrodes were attached to wires by
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25 using Silver Nano Paste (DGP, Advanced Nano Products, Korea). The wire connection with
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27 electrode was sealed with epoxy according to Zhang et al. (2009).
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34 The anode chamber was filled with 0.31 g/l NH_4Cl , 0.13 g/l KCl , 1.33 g/L acetate, $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$:
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36 4.22 gL^{-1} , $\text{Na}_2\text{HPO}_4\cdot\text{H}_2\text{O}$: 2.75 gL^{-1} , 12.5 mL mineral solution and vitamin solution (Zhang et al.,
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38 2009) and 25 ml was taken from the anode of a two-chamber MFC operating with acetate-modified
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40 domestic wastewater for half year and used as inoculum.
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44 The cathode chamber was filled with 50 mM ferricyanide solution $\text{K}_3\text{Fe}(\text{CN})_6$ in 50 mM
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46 phosphate buffer ($\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$: 4.22 gL^{-1} , $\text{Na}_2\text{HPO}_4\cdot\text{H}_2\text{O}$: 2.75 gL^{-1}) adjusted to pH 7.0 with 1 N
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48 NaOH (Zhang et al., 2009).
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51 The chambers were stirred by magnetic stirrer bars (250 rpm) and the experiments were run at
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53 room temperature (20 ± 5 °C). Twelve MFCs were set up for each pair of electrodes. The voltage was
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55 monitored by connecting the wires to a multimeter (Model 2700, Keithly Instruments, Inc.,
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Cleveland, OH, USA). The multimeter was connected to a computer that read and saved the voltage-results every 10 min. All the tests were performed in duplicate.

2.5 Visualization of nanoelectrodes

The topographies of the nanoelectrodes based on Si were visualized by using a Zeiss scanning electron microscope (SEM Zeiss). The carbon-based electrode was visualized by using Inspect™ line of SEM. To detect Au on the electrode surface, the program INCA analysed the spectra in the SEM-image.

2.6 Calculations

Voltage (V) was measured by a multimeter. A resistance (R) of 1000 Ω was used in all experiments and the power density (P_A) was calculated according to the equation:

$$P_A = \frac{V^2}{AR} \quad (1)$$

where, A is the surface area of the anode measured in m^2 (Logan, 2008). Each electrode had a projected area of 0.0009 m^2 .

3. Results and Discussion

A sketch of nanograss with conductive material is shown in Figure 1a. Ti, Cu and Au were chosen due to their low resistivity (4.2×10^{-7} , 1.7×10^{-8} , 2.4×10^{-8} $\Omega \cdot m$, respectively), while the resistivity of the HighSi and LowSi are 100 and 0.025 $\Omega \cdot m$, respectively. The same depositions were made on plain Si without nanograss (Figure 1b). Furthermore, the power production of electrodes made of gold nanoparticles on carbon-paper was also investigated (Figure 1c).

3.1 Resistances of electrodes

The resistance of the fabricated electrodes was measured in order to predict the performance of the electrodes in the MFC. Expanding the electrode surface area by forming nanograss on the electrodes, did not significantly lower their resistance (Table 1), but may provide more space for bacteria to attach. Modification of the electrode with nanograss may also alter surface

1 hydrophobicity and roughness, thus facilitating adhesion of bacteria. The carbon-paper sputtered
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3 with Au showed a lower resistance of 1.3 Ω than the 1.6 Ω of conventional carbon-paper. The
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5 lowest resistance of 0.5 Ω was measured on the LowSi coated with Cu and on the Si-electrode with
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7 Ti + Cu on both sides. It is worth mentioning that the resistances were measured on the deposited
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9 side and therefore there is no difference in these results between deposition on one side or on both
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11 sides. The high resistance of LowSi with the 40,000 Ω was lowered to below 10 Ω by deposition of
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13 either Cu, Ti or Au. This means that the resistance results were approximately within the range of
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15 carbon-paper which would ensure high power generation.
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20 *3.2 Expanding the surface area with nanograss increased electricity generation*

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22 Since Si has low conductivity, all nanograss formulations on Si (HighSi, LowSi, nanograss on
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24 HighSi and nanograss on LowSi control electrodes) showed low current output and no power
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26 density difference were observed with these electrodes. Even though Si is a semiconductor, the
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28 increase in specific surface area did not affect power generation (Fig. 3). Nanograss made of HighSi
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30 and LowSi can be seen in Fig. 2a and 2b.
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35 A maximum power density of 0.04 mW/m² was achieved with a plain Si electrode coated with Ti
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37 and Au. Ti and Au deposited on nanograss gave a maximum power density of 2.5 mW/m², but
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39 power generation decrease probably due to a lack of substrate (Zhang et al., 2009). The remarkably
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41 higher maximum power density, when depositing Ti and Au on nanograss than on plain Si,
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43 indicates that expanding the surface area can give higher power generation. The difference can be
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45 seen in Fig. 2h and 2f, where the deposited nanograss gives a larger area and thereby more space for
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47 the bacteria to attach. The achieved power density was not high, probably because of the high
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49 resistance of Si that reduces electricity production. Moreover, the electrodes were only coated from
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51 one side, which influenced power output. Accordingly, the electrodes deposited with Ti and Au on
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53 both sides gave a significant higher maximum power density of 86.0 mW/m². The power density
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1 reached a maximum value after 524 h whereas the carbon-paper electrode achieved its maximum
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3 value after about 400 h. The difference in lag time under these two conditions could be due to the
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5 different electrode structures leading to different electrochemical activities of the biofilm on the
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7 electrode surfaces. No power generation was observed in the control reactors where no inoculums
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9 were added (data not shown).
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11 12 13 *3.3 Copper deposition is not optimal for MFC-electrodes*

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15 The maximum power density values of plain Si coated with Cu, nanograssed plain Si coated with
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17 Cu and plain Si coated with Ti and Cu on both sides were 0.9, 0.6 and 0.04 mW/m², respectively
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19 (Fig. 5). Even though Cu has a low resistivity and the topography area was expanded with
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21 nanograss (Fig. 2c and Fig. 2d), power generation was low. A probable explanation for the low
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23 current for the Si coated with Cu was that during operation of the MFC, the Cu was crumbled and
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25 washed off the electrodes.
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29 30 31 *3.4 Enhanced electricity generation using gold nanoparticle electrodes*

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33 Carbon paper electrodes sputtered with Au nanoparticles and traditional carbon-paper electrodes
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35 were compared for electricity generation. To verify that gold nanoparticles were sputtered onto the
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37 carbon paper, an SEM-image was analyzed and a high concentration of gold was observed (Fig. S1
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39 and Fig. S2, Supplementary data).
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43 Carbon-paper with Au nanoparticles demonstrated a power density of 346.9 mW/m², which is
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45 2.9 times higher than that obtained with normal carbon-paper (119.6 mW/m²). What is also
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47 interesting is that normal carbon-paper reached its maximum power generation after 428 h, while
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49 gold nanofabricated carbon-paper reached its maximum value after 150 h, which is 2.85 times
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51 faster. Sputtering of carbon-paper with Au nanoparticles therefore an important step towards
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53 increasing MFC performance. The power density decreased to about 200 mW/m² in 100 h after
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55 reaching its maximum value, but this power density was still higher than the maximum power
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density achieved with the carbon paper electrode (Fig. 6). No power generation was observed in the control reactors without inocula (data not shown), indicating that the power generation was catalyzed by the bacteria in the anode. The power density obtained was higher than that observed previously (65 mW/m^2) in a MFC with carbon-cloth electrodes coated with carbon nanotubes (Tsai et al., 2009). The improvement in electricity generation with nanofabricated carbon paper was comparable to that observed in previous studies, in which graphite anodes decorated with Au or Pd nanoparticles produced 2 to 20 times higher current densities (74.4 and 8.8 mA/m^2 , respectively) than plain graphite anodes in the presence of *Shewanella oneidensis* MR-1 (Fan et al., 2010). The higher current density (620.8 mA/m^2) obtained in the present study could have been due to the use of carbon paper instead of a graphite disk which has relatively higher resistance and to the nanofabrication process employed. Overall, the above results indicate that Au nanoparticles on carbon paper enhanced power generation drastically compared to conventional carbon paper electrodes. Since carbon paper is cheaper than most of the electrode materials, nanofabrication based on carbon paper may greatly reduce the cost for future applications. The nanofabricated electrodes enable better utilizing of the power generation capability that an MFC can provide. Higher electricity generation efficiency and cheaper electrode materials may allow coupling of MFCs to wastewater treatment plants, achieving clean and renewable energy production on a large scale.

4. Conclusion

Nanograss-fabricated electrodes have the potential to improve the power output of MFCs. Ti and Au deposited on nanograss gave a maximum power density of 2.5 mW/m^2 , which was almost 63 times higher than that of a plain Si electrode coated with Ti and Au. Furthermore, the power density was improved 2.9 times by sputtering carbon paper electrodes with Au nanoparticles. With further developments in nanotechnology, it should be possible to fabricate nanograss on both sides of a Si

1 electrode or on a more conductive electrode, which may make the application more efficient and
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3 cost-effective.
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List of tables and figures with their legends:

Table 1. Performance of MFCs with different electrodes

Fig. 1. Schematic representation of nanofabricated electrodes. a) Nanograss etched in silicium and coated with conductive material resulting in larger surface area due to the folding. b) Plain silicium coated with conductive material achieving a conductive layer on the Si-template. c) Carbon paper sputtered with gold nanoparticles.

Fig. 2. SEM images of nanoelectrodes. a) LowSi + Nanograss, b) HighSi + Nanograss, c) Nanograss + Cu, d) Nanograss + Cu zoom in, e) Nanograss + Ti + Au, f) Nanograss + Ti + Au zoom in, g) LowSi + Cu, h) LowSi + Ti + Au

Fig. 3. Power density curves for different Si electrode. a) Plain high resistivity Si electrodes. b) Plain low resistivity Si electrodes. c) Nanograss on high resistivity Si electrodes. d) Nanograss on low resistivity Si electrodes.

Fig. 4. Power density curves of Si electrodes coated with Ti and Au. a) Ti and Au deposited on plain Si electrodes. b) Ti and Au deposited on nanograss electrodes. c) Ti and Au deposited on both sides of plain Si electrodes.

Fig. 5. Power density curves of Si electrodes coated with Ti and Cu. a) Cu deposited on plain Si electrodes. b) Cu deposited on nanograss electrodes. c) Ti and Cu deposited on both sides of plain Si electrodes.

Fig. 6. Power density curves of a) carbon-paper electrodes as control and b) carbon paper electrodes sputtered with Au nanoparticles.

Table 1 Performance of MFCs with different electrodes

Electrode type	Deposition	Deposition layer (nm)	Resistance (Ω)	Max. Power Density (mW/m^2)
Carbon-paper	Control	-	1.6	119.6
	Gold	-	1.3	346.9
	Control	-	40 000	0.002
	Copper	100	0.5	0.9
	Titanium + Gold	10 + 100	1.0	0.04
LowSi	Titanium + Copper (both sides)	10 + 100 (each side)	0.5	0.04
	Titanium + Gold (both sides)	10 + 100 (each side)	1.0	86.0
	Control	-	8.5	0.0001
LowSi + Nanograss	Copper	100	6.7	0.6
	Titanium + Gold	10 + 100	3.0	2.5
HighSi	Control	-	200 000	0.03
HighSi + Nanograss	Control	-	200 000	0.01

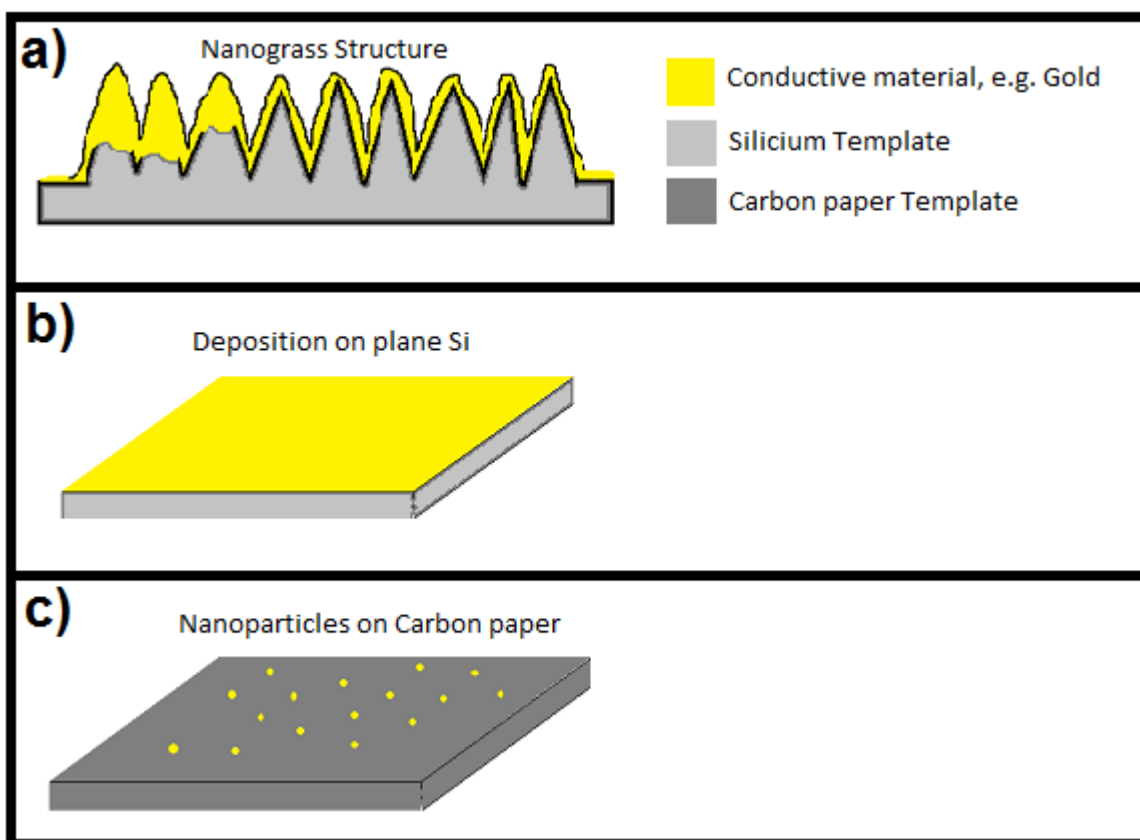


Fig. 1

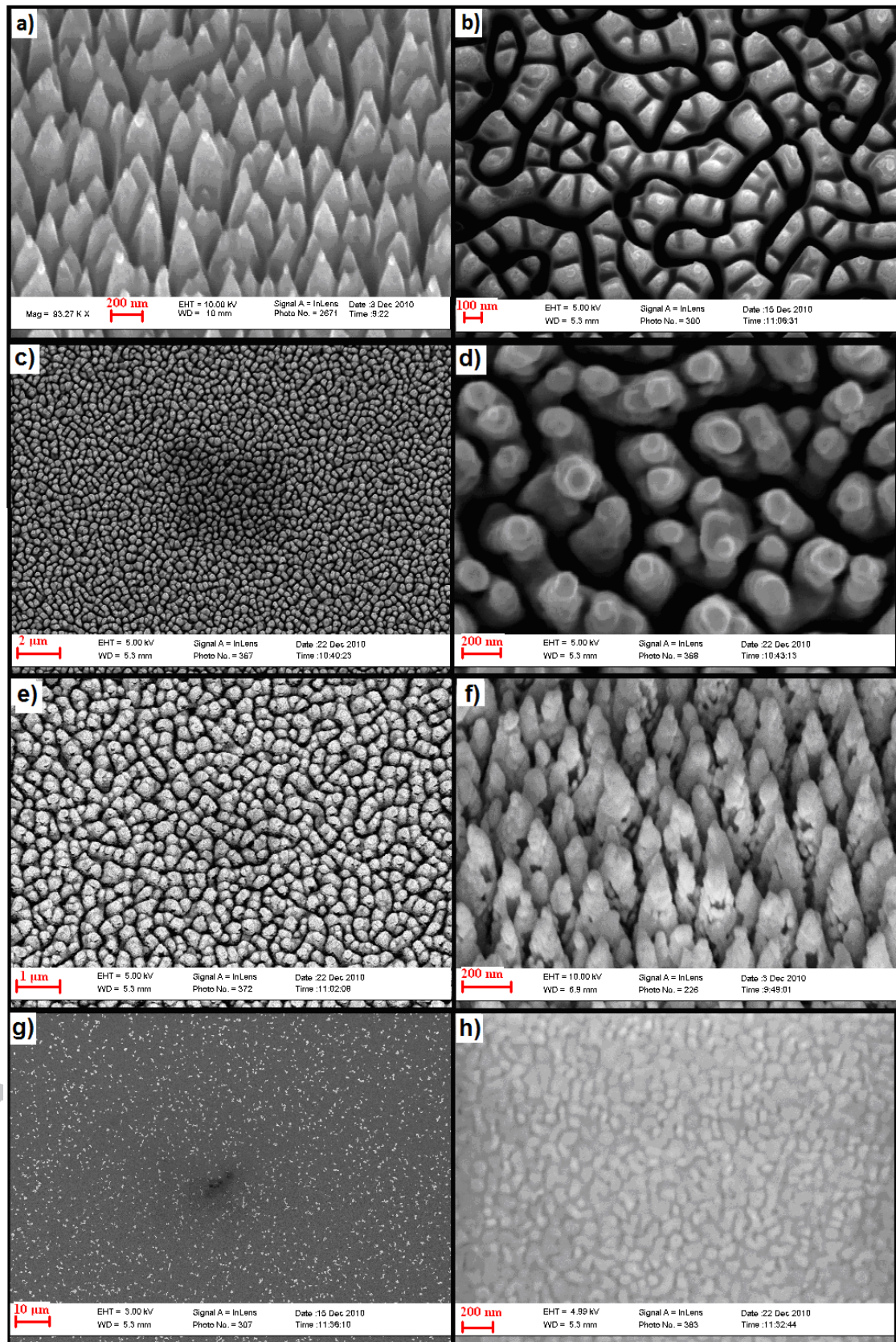


Fig. 2

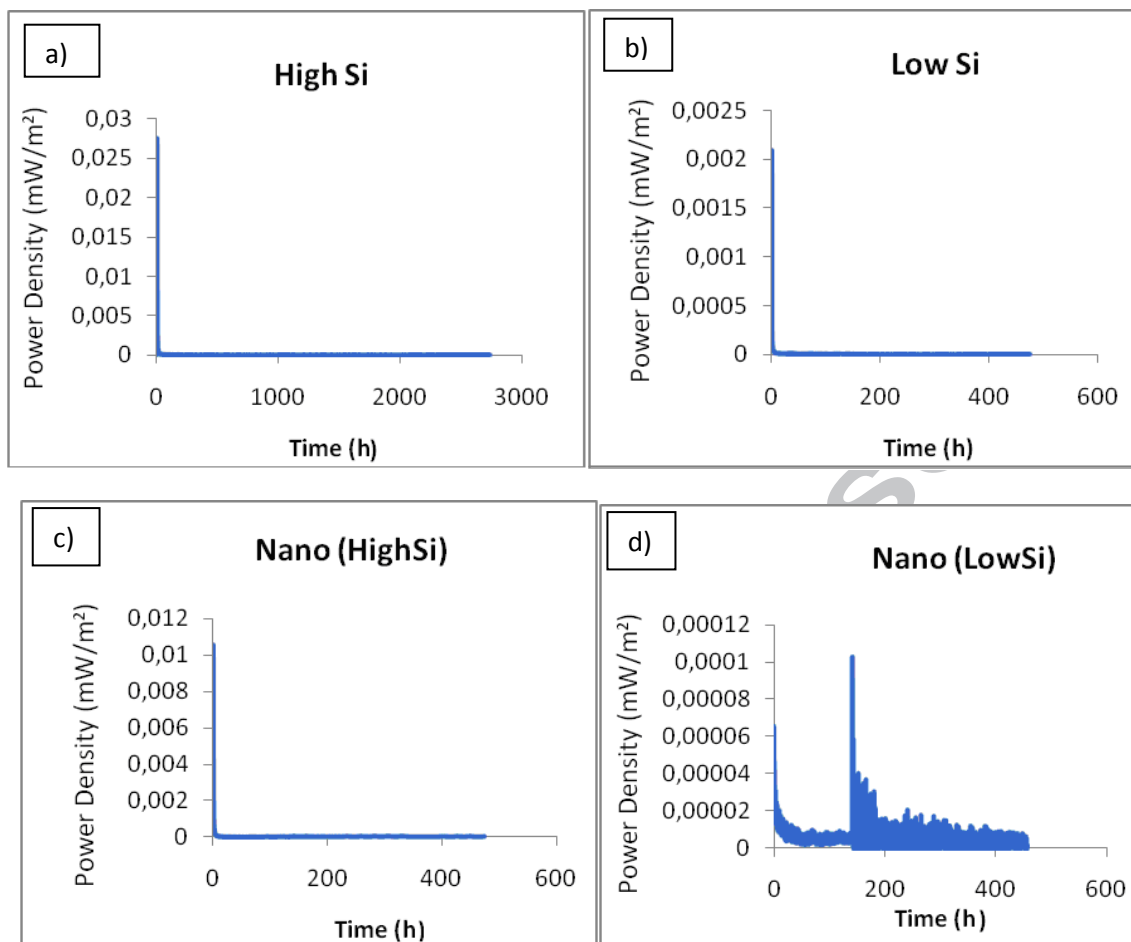


Fig. 3

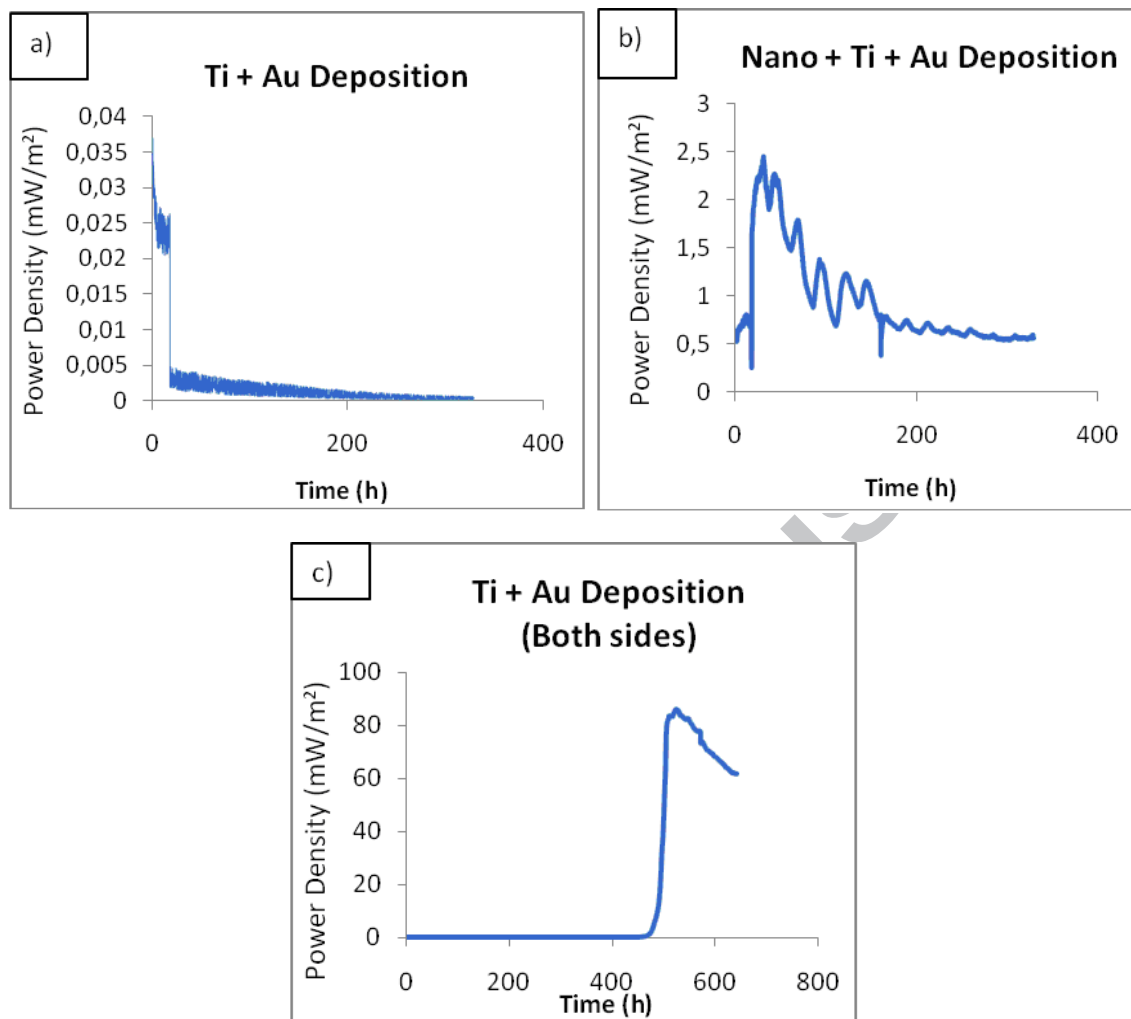


Fig. 4

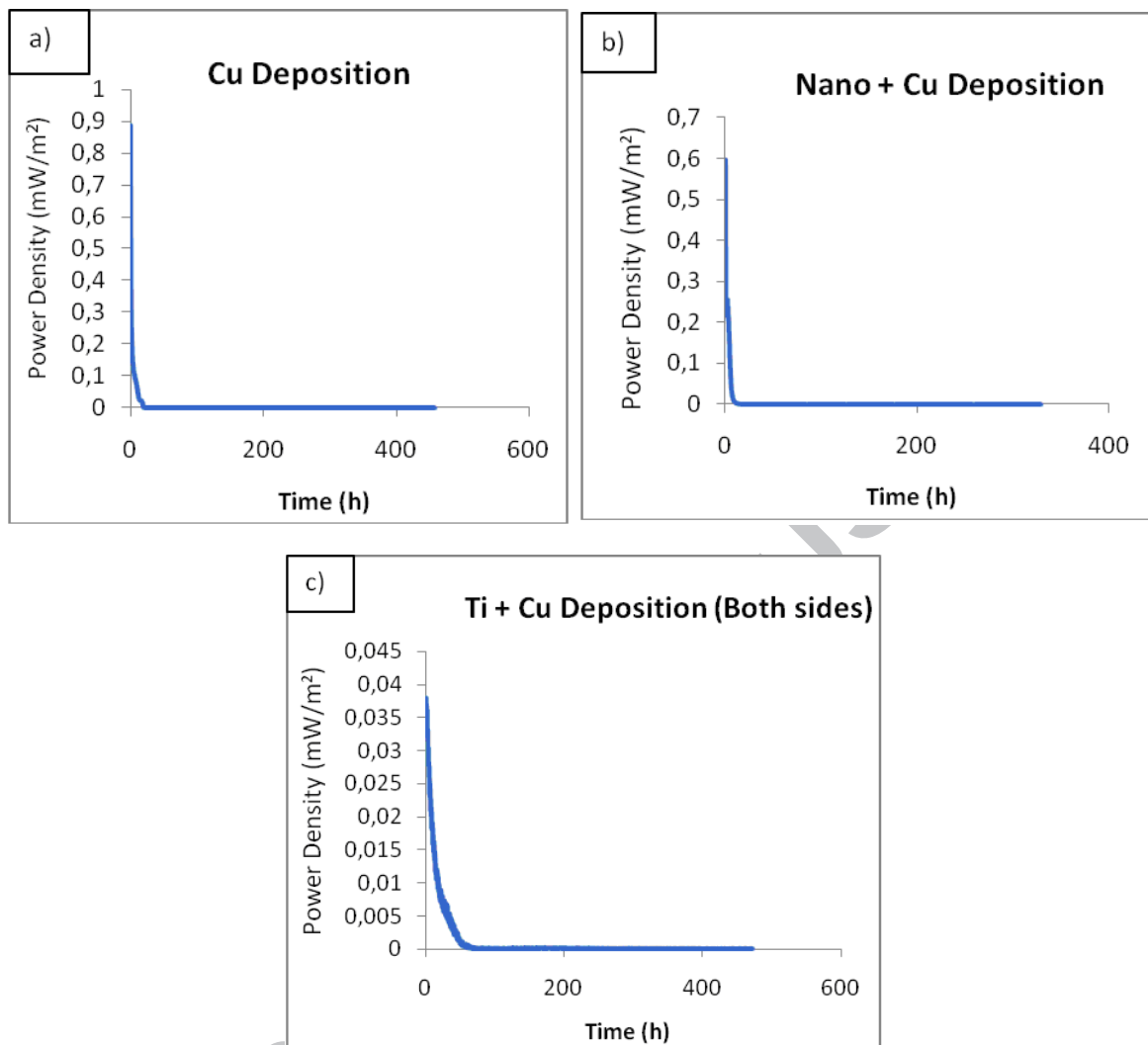


Fig. 5

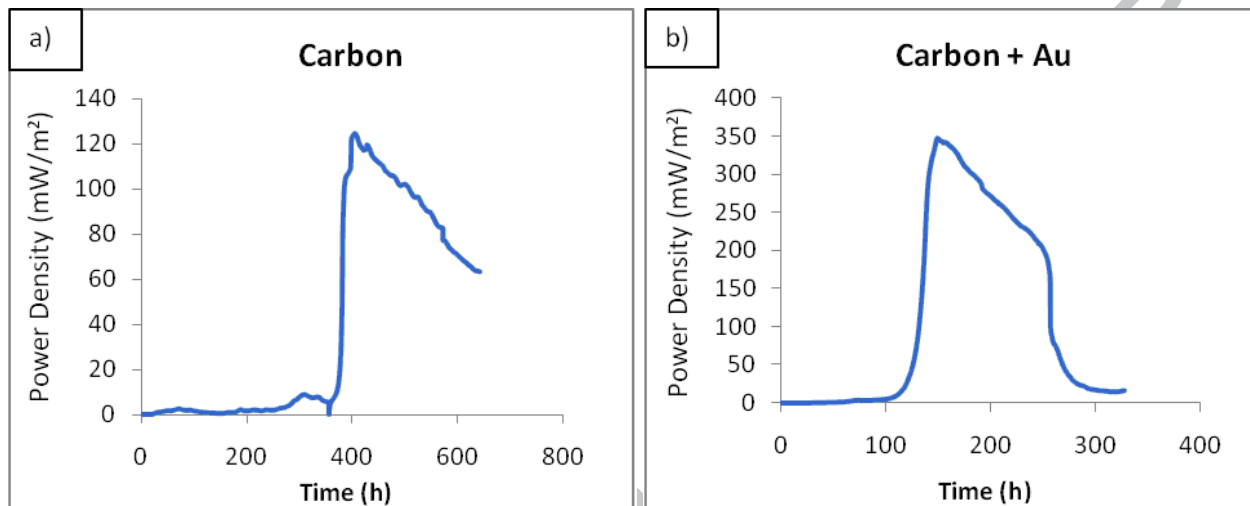


Fig. 6

Highlights

- Improvement of power generation using electrodes with grass-like nanostructures
- Ti and Au deposited on nanograss produced 63 times higher power than the control
- Carbon paper sputtered with Au particles increased the power generation drastically