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# Development of Polymeric Porous Membrane for Mediator-Less Microbial Fuel Cells: An Electrochemical Study

## Abstract

In this work, gold nanoparticles (AuNPs) are embedded on the proton exchange membrane in a straightforward manner and are made highly stable. Nanoparticles provide high surface-to-volume ratio with excellent biocompatibility, using appropriate ligands, which allows for a biocompatible environment for bacterial functions. High conductivity, high surface area and catalytic properties of AuNPs make them excellent materials for MFCs. We employed layer-by-layer (LbL) self-assembly technique to prepare multilayered thin-films of polycation poly(allylamine hydrochloride) (PAH) and negatively functionalized AuNPs. The (PAH/AuNP) thin-films act as the catalyst layers and are to provide means for high porosity and high electrical conductive in the LbL thin-films when the polycation serve to assist LbL thin-film formation through ionic bonds. Scanning electron microscopy was used to investigate the morphology and nano/microstructure of the porous membrane catalyst. Samples consisting of different thickness thin-films were tested for their performance over five-day periods. Bioelectricity was generated using *Shewanella oneidensis* MR-1 cultivated on organic substrate with trypticase soy broth medium. Trypticase soy broth and ferricyanide were injected into the anode and cathode chambers as anolyte and catholyte respectively. Generated voltage and current were monitored and recorded using LabView through NI-DMM, over five-day periods.

## Keywords

microbial fuel cell, proton exchange membrane, *shewanella oneidensis* MR-1, poly(dimethylsiloxane), gold nanoparticles

## Disciplines

Membrane Science | Other Mechanical Engineering | Petroleum Engineering

## Comments

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### DEVELOPMENT OF POLYMERIC POROUS MEMBRANE FOR MEDIATOR-LESS MICROBIAL FUEL CELLS: AN ELECTROCHEMICAL STUDY

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#### ABSTRACT

In this work, gold nanoparticles (AuNPs) are embedded on the proton exchange membrane in a straightforward manner and are made highly stable. Nanoparticles provide high surface-to-volume ratio with excellent biocompatibility, using appropriate ligands, which allows for a biocompatible environment for bacterial functions. High conductivity, high surface area and catalytic properties of AuNPs make them excellent materials for MFCs. We employed layer-by-layer (LbL) self-assembly technique to prepare multilayered thin-films of polycation poly(allylamine hydrochloride) (PAH) and negatively functionalized AuNPs. The (PAH/AuNP) thin-films act as the catalyst layers and are to provide means for high porosity and high electrical conductive in the LbL thin-films when the polycation serve to assist LbL thin-film formation through ionic bonds. Scanning electron microscopy was used to investigate the morphology and nano/microstructure of the porous membrane catalyst. Samples consisting of different thickness thin-films were tested for their performance over five-day periods. Bioelectricity was generated using *Shewanella oneidensis* MR-1 cultivated on organic substrate with trypticase soy broth medium. Trypticase soy broth and ferricyanide were injected into the anode and cathode chambers as anolyte and catholyte respectively. Generated voltage and current were monitored and recorded using LabView through NI-DMM, over five-day periods.

**Keywords:** Microbial fuel cell; Proton exchange membrane; *Shewanella oneidensis* MR-1; Poly(dimethylsiloxane); Gold nanoparticles

#### INTRODUCTION

With the ever growing need for energy and pollution concerns, demand for clean energy is increased worldwide. Microbial fuel cells (MFCs), as a new approach toward clean energy, has attracted much attention in the recent years. Many research groups and scientists all over the world have dedicated their resources to this field. MFC is a device that converts chemical energy to electrical energy by the reaction of microorganisms. Despite these challenging efforts, this device has not been yet commercialized. MFCs devices enable direct conversion of biochemical energy to electrical energy, using bacteria. Bacteria are the catalysts in the oxidization process of inorganic and organic matters. Finally, this process yields to the generation of current in the MFCs[1]. We have previously shown that polymers, metal nanoparticles, and their composites can be deposited on functionalized substrates as catalyst layers using LbL deposition[2-8]. We have also demonstrated the influence of the nano and micro structures of thin-films on the electrical and ionic properties of the electrodes, catalyst layers and functionality of MEMS devices[9-25]

MFCs technology has some advantages over the other techniques which apply for power generation from organic matters. The whole process could be completed at ambient temperature and conditions. These working temperatures could be identified as major benefits of the MFCs comparing to other available bioconversion systems which usually operate at high temperatures. In addition, the process of power generation in MFCs is direct; thus the efficiency is high. Another advantage is related to extensive applications of this kind of fuel cells. They have potential for water treatment[26], desalination[27], hydrogen generation[28], wastewater treatment[29, 30] and also, environment monitoring applications[31].

Qian et al. [32], reported a new microfluidic microbial fuel cell platform built by soft-lithography techniques. They designed a unique sub-5  $\mu\text{L}$  polydimethylsiloxane soft chamber featuring carbon cloth electrodes and microfluidic delivery of electrolytes. Bioelectricity was generated using *Shewanella oneidensis* MR-1 based minimal medium. These micro-MFCs exhibited fast start-ups, reproducible current generation, and enhanced power densities up to  $62.5 \text{ W m}^{-3}$  from sub-100  $\mu\text{L}$  MFCs.

Different strains of *Shewanella putrefaciens* bacteria have the ability to be used in the MFCs. In the research conducted by Kim et al. [33], they examined MR-1, IR-1, and SR-21, which all of them were grown in anaerobic condition, by cyclic voltammetry (CV) technique. They came to this conclusion that these anaerobically grown cells have electrochemical activity. They also do the same experiments on cell suspensions which were grown in aerobic condition and the results were completely opposite.

On the other hand, metal nanoparticles are widely used in microelectronics, photo catalyzes, magnetic devices, chemisorption, aerosols, and powder metallurgies because their strong potential ability[34]. Among all the metal nanoparticles, gold nanoparticles (AuNP) have been extensively studied in the literature. Many techniques have been exploited to prepare shape-controlled AuNPs.

AuNPs possess unique physical and chemical properties that make them excellent scaffolds to be the electrode in the fuel cell[35]. First of all, AuNPs can be synthesized in a straightforward manner and it can be stable adsorption layer. Then they provide surface-to volume ratio with good biocompatibility, which possess a higher conductivity as electrode in fuel cell. Third, according to the chemical environment, AuNPs has the ability to vary their shape and size for the reaction. Many researchers studying PEM reactors, including us, have suggested that AuNPs feature excellent conductivity, high surface area and catalytic properties that make them excellent materials for the electrochemical detection with microbial[35]. In contrast, the use of AuNP Nafion membrane has not been involved in microbial fuel cell, which leads the AuNPs be the electrode and replace the carbon cloth electrode. In addition, consider the coefficient power value of the chamber size, as the small chamber designed, the higher power density is easier to achieve[32]. Finally, we designed a micro-MFC to incorporate AuNP Nafion membrane into a sub-300  $\mu\text{L}$  chamber embedded with 60mm thickness polydimethylsiloxane (PDMS) frame.

Performance of microbial fuel cells is a function of porosity and conductivity of the catalyst layers. Ultra-thin porous-conductive catalyst layers can improve initiation time and performance of MFCs through increased electron conductivity. Porosity of the catalyst layers allows and ensures biological

functions and activities of the bacteria. Here we report a novel class of MFCs with a new AuNP doped proton exchange membrane. Functional AuNPs can provide distinct physical and chemical attributes that support chemical and biological functions of the bacteria.

## EXPERIMENTAL METHODOLOGY

### 1. AuNP-Nafion membrane (PAH/AuNPs thin-film)

Nafion membranes of thickness 25  $\mu\text{m}$  (Ion Power, Inc.) were used as the ionomeric membrane and the AuNPs thin-film was the catalyst layer in the MFC. (Fig.1) Nano-composites of the polycation poly(allylamine hydrochloride) (PAH, Sigma Aldrich) and anionic functionalized AuNPs, ( $\sim 3 \text{ nm}$  diameter, Purest Colloids, Inc.) were deposited on both sides of the Nafion membrane via Layer-by-Layer deposition. Nafion membranes were extended on the substrates. Every 5 minutes, the substrates were alternately immersed each in aqueous solutions of PAH (concentration of 10 mM) and AuNPs (20 ppm concentrations) with three rinsing steps for 1 minute each in deionized water after each deposition to get one PAH/AuNPs bilayer. Repeating the above process for 20 times will result in a 20 bilayers PAH/AuNPs thin-film, which we used for our experiments.

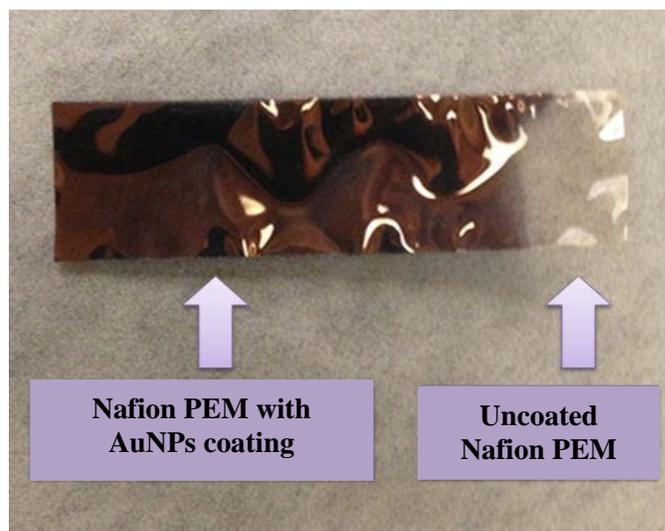


Figure1. AuNP Nafion membrane

### 2. Chemical and Agential

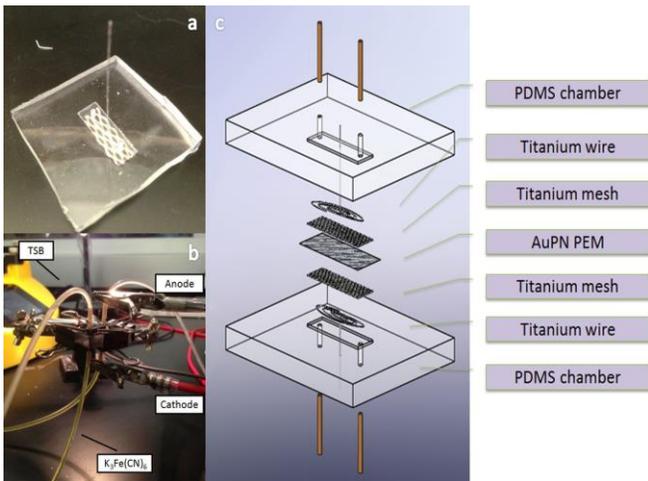
The chemicals used in the experiment includes: anionic functionalized AuNPs ( $\sim 3 \text{ nm}$  diameter, Purest Colloids, Inc.), Nanocomposites of the polycation poly(allylamine hydrochloride) (PAH, Sigma Aldrich), Nafion® membrane (Nafion® 115, Ion Power, New Castle, DE), 184 silicone elastomer (Dow Corning, Midland, MI), 1.25" inner diameter polyethylene tubing (Dow Corning, Midland, MI), Diagnostic Systems, Sparks, MD), phosphate buffered saline (Sigma Aldrich, St. Louis, MO), Ferricyanide catholyte (50 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ ).

### 3. Bacterial strain and culture

*S. oneidensis* MR-1 was chosen as the electron-generate bacteria due to its stable and efficient generating capacity[1]. A solid medium plate which was made by trypticase soy broth (TSB) and agar need to prepare for culture the bacterial. Then MR-1 was scraped on plate and let it grow with 37 °C for 12-24 hours. After culture, transfer the plate in the refrigerator for preservation. The bacteria were soaked into syringe by liquid TSB and the mixture solution was injected into MFC for generation of electricity.

### 4. PDMS chamber

Two 12×5×0.45mm<sup>3</sup> pieces of PDMS were used as the reaction chamber. Sylgard 184 elastomer and curing agent was mixed with 10:1 ratio to pour onto a 12×5×0.45mm<sup>3</sup> rectangular steel bar as the chamber mold, which is attached to the bottom of a dish. The dish was then heated in oven for 15-20mins at 85 °C to cure PDMS. Two polyethylene tubing were connected to the punched holes through the chamber.



**Figure 2. (a) Titanium wires were knitted on the titanium mesh and throughout from chamber. (b) Ferricyanide ca-tholyte was injected with a 150μL/h. (c) MFC device was constructed as sandwiching with AuNP Nafion membrane, titanium meshes and PDMS chambers.**

### 5. Assembling of MFC

The MFC device was constructed as sandwiching by 4 clips from each side with AuNP Nafion membrane, titanium meshes and PDMS chambers (Fig. 2c). In this MFC design, AuNPs which have formed a thin layer on the Nafion were the actual catalyst. The titanium meshes were functioned as the wire to extend on the surface AuNP Nafion membrane. Two titanium wires were knitted on the titanium mesh and throughout from top and bottom part of PDMS chamber. (Fig. 2a)

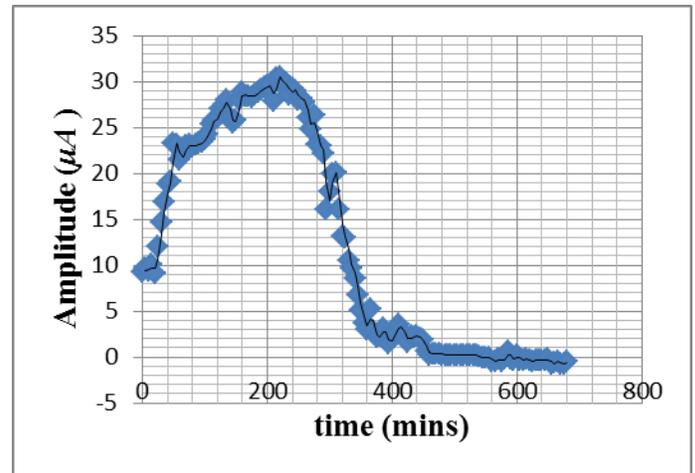
The entire MFC was disinfecting into autoclave at 120 °C for 15 minutes. Before the injection, the syringe with bacteria was

warmed up to 37 °C in incubator for 5 minutes. Then a 10k Ω resistor was connected in series with MFC. A syringe full of Ferricyanide ca-tholyte (50mM K<sub>3</sub>Fe(CN)<sub>6</sub> in a 100mM pH 7.4 phos-phate buffered saline) was injected into chamber with a constant speed of 150μL/h by syringe pump. (Fig. 2b) The entire MFC was operated at ambient condition.

The voltage was recorded by DMM as a continue function of time. Current was auto calculated in Lab View by Ohm's law  $I=V/R$ . Power density was calculated by anode area of chamber.

### RESULTS AND DISCUSSION

A 10kΩ resistor was added parallel to the circuit to determine the voltage and current generated by MFC. Before injection of bacteria into the chamber, a background current of 4nA was observed when only TSB medium and Ferricyanide ca-tholyte were present in the chamber. After the injection of *Shewanella oneidensis* MR-1, the current increased to 10μA and keep increasing for 220 minutes until it reached the peak value of 31μA then decreased to 50% in 90 minutes and close to 5% by 240minutes. The current then remained at a constant value of approximately 0.5μA. (Fig. 3)



**Figure 3. This graph shows current vs. time starting from thirty five hours after introduction of *Shewanella MR-1* into the device**

The current remained above the start value of 10μA for 330 minutes and more than 200 minutes above 20μA. Implying that the MFC device can supply an effective voltage of 200mV for over 250 minutes per injection. Normalizing the current density for 60 mm<sup>2</sup>, the area of the anode, the maximum current density of MFC presented in this research is 50μA/cm<sup>2</sup>. This is a significant improvement compare to the previously reported current densities of micro-MFCs (10μA/cm<sup>2</sup> and 13μA/cm<sup>2</sup>)[18, 32]. We have shown that MFCs based on AuNP coated Nafion membranes exhibit higher current density which is due to enhanced conductivity, chemical and biological reactions.

AuNPs can provide distinct physical and chemical attributes that support chemical and biological reactions. Firstly, AuNPs can be synthesized in a straightforward manner and can be made highly stable on Nafion membrane. Secondly, they provide high surface-to-volume ratio with excellent biocompatibility using appropriate ligands[35].

## CONCLUSION

A PDMS-based with a 60 mm<sup>2</sup> reaction area work with an AuNP Nafion membrane can provide maximum 31 $\mu$ A current and 50 $\mu$ A/cm<sup>2</sup> current density. LbL self-assembly technique to prepare a multi-layered membrane with AuNPs can significantly improve the conductivity. The micro-MFC chamber was easy to build and the device is convenient to fabricate. It is demonstrated that *Shewanella Oneidensis* MR-1 as the generated microorganism can produced current peak and contained the valid current for 300 minutes.

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