Nanoparticle decorated anodes for enhanced current generation in microbial electrochemical cells

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ABSTRACT

The development of highly efficient anode materials is critical for enhancing the current output of microbial electrochemical cells. In this study, Au and Pd nanoparticle decorated graphite anodes were developed and evaluated in a newly designed multi-anode microbial electrolysis cell (MEC). The anodes decorated with Au nanoparticles produced current densities up to 20-fold higher than plain graphite anodes by Shewanella oneidensis MR-1, while those of Pd-decorated anodes with similar morphologies produced 50–150% higher than the control. Significant positive linear regression was obtained between the current density and the particle size (average Feret’s diameter and average area), while the circularity of the particles showed negative correlation with current densities. On the contrary, no significant correlation was evident between the current density and the particle density based on area fraction and particle counts. These results demonstrated that nano-decoration can greatly enhance the performance of microbial anodes, while the chemical composition, size and shape of the nanoparticles determined the extent of the enhancement.

1. Introduction

Widely available fuel sources and moderate operational conditions make microbial electrochemical cells, such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), very promising for renewable energy generation, wastewater treatment, and use for bioremediation. However, no comprehensive study has been performed on the effects of nanoparticles with different chemical compositions on the performance of microbial electrochemical cells. Recent studies have demonstrated that CNT decorated anodes enhanced the power generation of MFCs (Qiao et al., 2007; Sharma et al., 2008). However, no comprehensive study has been performed on the effects of nanoparticles with different chemical compositions and morphologies on the anode performance of MFCs or MECs.

In this study, we decorated graphite disks with gold (Au) and palladium (Pd) nanoparticles, which were used as anodes in a multi-anode MEC for current generation. The relationships between the current density and the properties of the anode surface, including the chemical composition, size (Feret’s diameter, average area), shape (circularity), and density (area fraction, particle counts) of nanoparticles, were investigated.

2. Experimental

2.1. Preparation of nanoparticle decorated anodes

Recent advances in nanofabrication provide a unique opportunity to develop efficient electrode materials due to the remarkable structural, electrical, and chemical properties of nanomaterials, such as nanoparticles and carbon nanotubes (CNTs). It is of great interest to examine the impact of changes in surface morphology and chemistry brought by nanomaterials on the performance of microbial electrochemical cells. Recent studies have demonstrated that CNT decorated anodes enhanced the power generation of MFCs (Qiao et al., 2007; Sharma et al., 2008). However, no comprehensive study has been performed on the effects of nanoparticles with different chemical composition and morphologies on the anode performance of MFCs or MECs. In this study, we decorated graphite disks with gold (Au) and palladium (Pd) nanoparticles, which were used as anodes in a multi-anode MEC for current generation. The relationships between the current density and the properties of the anode surface, including the chemical composition, size (Feret’s diameter, average area), shape (circularity), and density (area fraction, particle counts) of nanoparticles, were investigated.

Superfine isomolded graphite disks (ø 1.6 cm × 0.5 cm, GraphiteStore.com, Inc.) were polished with ultrafine sand paper (2000 grit, 3 M Company) and used as the substrates for the
growth of nanoparticles and as the control in each test run. Au and Pd thin films were deposited on the polished graphite disk using sputter coating for 0.5–1 min. Au and Pd nanoparticles with various morphologies were synthesized by thermal annealing of the thin films by placing the samples in a quartz tube and heating them between 600 and 800 °C for 15–45 min.

2.2. Bacterial species and culture conditions

*Shewanella oneidensis* MR-1 (ATCC 700550) was cultured aerobically with a medium containing 30 g Trypticase Soy Broth per litter (BD 211825, Becton, Dickinson Company) at 30 ± 1 °C. The MEC was inoculated with 30 ml cell culture at early stationary phase (optical density at 600 nm of 1.2–1.3). Phosphate (0.1 M, pH 7) was used as a pH buffer and to reduce the internal resistance of the MEC. Sodium lactate (final concentration 30 mM) was added as an electron donor in the MEC.

2.3. MEC construction and operation

An MEC with removable multiple anodes was constructed and used to evaluate the nano-structured anodes. The multi-anode configuration allows the biofilm development on the anodes under exactly the same condition and thus minimizes the effect of the variation in inoculum concentration, media composition and cathode performance on current generation. The MEC is sealed and can be autoclaved so that an anaerobic and sterile environment can be maintained. A schematic and a photograph of the MEC are shown in Fig. 1. The cathode was made of wet-proofed (30%) carbon cloth (type B, E-TEK Division, Inc., USA) coated with Pt/C (20%, E-TEK Division, Inc., USA) following our previous reported procedures (Liu et al., 2005). The final platinum loading was 0.5 mg/cm² per projected cathode area. The nanoparticle decorated graphite disks were used as anodes. The size of the cathode (10 cm × 15 cm) was more than 25 times larger than the total effective area of the 8 anodes (0.7 cm² × 8) so they did not limit the performance of the MEC system. The short electrode spacing (1.7 cm) and high buffer concentration (0.1 M phosphate buffer) were also used in the MEC design to reduce the internal resistance. After the MEC was inoculated with early exponential phase cultures of *S. oneidensis*, a voltage of 0.6 V was applied to the MEC. A multimeter with a data acquisition system (2700, Keithly, USA) was used to monitor the current change by measuring the voltage drop through a resistor. The current generation of the eight anodes was monitored separately. The maximum hourly average current density was calculated between 5 and 65 h after inoculation to indicate the best performance in the tested condition while filtering the temporary fluctuation of the recorded data.

2.4. SEM and image processing

The morphologies of the nanoparticle decorated electrodes were examined using an FEI Sirion field emission scanning electron microscope (FE-SEM) with amplification ranging from 8000 × to 64,000 ×. To quantify the size, shape and density of the irregular nanoparticles, the SEM images with 32,000 × amplification were processed with ImageJ (Ver. 1.41, NIH, USA) to compute the total number of particles (particle count), total area, area fraction, and the area, circularity, and Feret’s diameter of each particle, excluding the ones on the edges. Area fraction is defined as the ratio of total particle area over the imaged electrode surface area. Feret’s diameter is the longest distance between any two points along the boundary of the particles. Only the particles larger than 700 nm² in surface area (30 nm in diameter for round particles) were considered in the calculation due to the large errors in computing these parameters for particles smaller than 700 nm² for a 32,000 × image. An example of processing the SEM image is shown in Fig. 2. The average Feret’s diameter, average area, and average circularity of

![Fig. 1. Schematic (a) and photo (b) of a prototype MEC with removable anodes. Cathode is common to all 8 anodes. The geometry is selected to allow consistent electrical field to form across each anode and improve consistency of data.](image)

![Fig. 2. The SEM of graphite anodes decorated with Pd (A) and Au (B) nanoparticles and the processed image of (B) using ImageJ (C).](image)
the largest particles covering 10% of the electrode surface were further calculated using Microsoft Excel (2003) to investigate the correlation between current density and particle size/shape. The 10% was chosen because the nanoparticles covered 11–22% of the electrode surface for all the tested samples.

3. Results and discussion

3.1. Enhanced current generation using nanoparticle decorated electrodes

Enhanced current output was demonstrated for all the nanoparticle decorated electrodes, including 11 Au decorated anodes and 5 Pd-decorated anodes. The Au decorated anodes generated a maximum current density ranging from 10.7 to 74.4 $\mu$A/cm$^2$, which was 2–20 times higher than the plain graphite anodes (control) (3.6 $\mu$A/cm$^2$). The Pd-decorated anodes produced an average current density ranging from 5.7 to 8.8 $\mu$A/cm$^2$, which was 50–150% higher than the control electrodes. Fig. 3 shows the enhancement of current generation with 4 of the nanoparticle decorated anodes.

The exact mechanisms for this enhanced current generation are still unclear. Our experimental results demonstrated that no considerable current was produced before the inoculation of $S$. oneidensis. The lack of oxidation and reduction peaks in cyclic voltammograms of nanoparticle modified anodes in media solutions also indicated that neither lactate nor other metabolites of $S$. oneidensis can be directly oxidized on the nanomodified anodes. Therefore, the significant difference in current generation was mainly caused by the enhanced electron transfer efficiency. They might also create a large surface for mediators to shuttle electrons from bacterial intracellular enzymes. In addition, enhancement of current generation could occur through modifications in cellular regulation driven by surface geometry or electrical properties. Our gene expression study shows that a selection of metabolic, structural, respiratory and regulatory genes were induced following exposure to nanoparticles (unpublished results). Nanomodification of the anodes may also alter the surface hydrophobicity and surface roughness, thus facilitating the adhesion or colonization of bacteria (Grivet et al., 2000; Emerson et al., 2006).

Figs. 4–6 also demonstrated that the Au decorated anodes generated much higher current densities than the Pd-decorated anodes with similar particle size, density and shape. For example, the current density was 74.4 $\mu$A/cm$^2$ for an Au anode with a particle size of 0.35 $\mu$m$^2$, which is 9-fold higher than that of the Pd anode with a particle size of 0.33 $\mu$m$^2$. The better conductivity of Au ($4.88 \times 10^7$ Sm$^{-1}$) than Pd ($9.48 \times 10^6$ Sm$^{-1}$) may contribute to the better performance of the Au modified anodes. The chemical composition or the type of nanoparticles might also affect the surface heterogeneity of the electrodes, including hydrophobicity and surface charge.

Fig. 5 shows the relationship between the maximum current densities and the average circularity of Au (solid diamonds) and Pd (open circles) particles.

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Fig. 4. Relationship between the maximum current densities and the average Feret’s diameter (A) and average area (B) of Au (solid diamonds) and Pd (open circles) particles.
ity and respiration functions of the cell (Panacek et al., 2006). TiO₂ nanoparticles, however, aid in biofilm resistance by forming a more hydrophilic surface (Yang et al., 2007). Various studies have shown the potential nano-toxicity (Hoet and Boczkowski, 2008) and antimicrobial activity of nanoparticles (Qi et al., 2004; Morones et al., 2005; Weir et al., 2008). On the other hand, some studies indicate that some nanomaterials, especially carbon nanotubes, can increase the biocompatibility and the electricity generation in MFCs (Morozan et al., 2007; Sharma et al., 2008; Zou et al., 2008; Tsai et al., 2009). The significant difference in current generation for Au and Pd nanoparticle decorated anodes with similar textures indicated that surface chemical properties are a critical factor affecting the electron transfer from bacteria to electrode.

### 3.2. Effect of particle size on current output

Significant positive linear correlation was obtained between current densities and the average Feret’s diameter, as well as the average area of the Au nanoparticles (Fig. 4). The current density increased from 10.7 to 74.4 μA/cm² with the increase of average Feret’s diameter from 174 to 972 nm and the average area from 0.02 to 0.035 μm². The significant enhancement of the current generation with Au nanoparticle sizes larger than 200 nm in diameter was possibly due to the increased direct contact between bacterial cells and the large particles, considering the size of a S. oneidensis MR-1 cell is about 1–2 μm in length and 0.5 μm in diameter. For Pd nanoparticle decorated anodes, however, no significant enhancement in current generation was observed with the increase of particle diameters and area, further indicating the importance of the chemical composition of nanoparticles. It has been reported that Ag nanoparticles less than 10 nm are more toxic to bacteria than larger particles (Morones et al., 2005; Gogoi et al., 2006). In this study, however, no inhibition was observed in current generation of S. oneidensis for Au particles ranging from 1 to 1000 nm.

### 3.3. Effect of particle shape on current generation

A negative correlation was observed between the current densities and average particle circularity (Fig. 5). The shape of nanoparticles might affect the nanoparticle–cell interactions (Verma and Stellacci, 2010). Pal et al. (2007) found that triangular silver nanoparticles were more toxic to Escherichia coli than rod or spherical nanoparticles. More possibly, the reason for the decrease of current with the increase in circularity is that the particles with different circularity/shape may have different crystal structures and surface chemistry, which affected the interactions between the bacteria and the electrode. The other possible reason is that the particles with smaller circularity (less roundish) tended to have larger Feret’s diameter and surface area, thus enhancing current generation for the respective anodes. It should be noticed that circularity might be only the indicator of other properties of nanoparticle, not the direct cause for the difference in current generation. Further studies are needed to elucidate the mechanism behind the apparent relationship between circularity and current generation.

### 3.4. Effect of particle density on current generation

In addition to the size and shape of the particles, the density (or the particle count and total area of the particles on the electrode surface) may also affect the roughness of the electrode surface and the adhesion force or wettability between the bacteria and the electrode (Emerson et al., 2006). To study the significance of particle density, we counted the particle number from the SEM images and calculated the area friction (the percentage of area covered by particles) of all the particles with a surface area larger than 700 nm² (about 30 nm in diameter for round particles). No significant linear regression between area friction and maximum current density was observed (Fig. 6A). Although a slightly negative correlation was found between the average current generation and the particle counts (Fig. 6B). It might be simply due to the correlation between particle size and particle counts. The samples with larger particles tend to have a smaller number of particle counts ($R^2 = 0.6218$ between the average Feret’s diameter and particle counts, $n = 11$).

### 3.5. Implications

This study demonstrated that nanostructures have potential to greatly enhance the performance of microbial anodes. An up to 20-fold increase in current has been achieved using Au nanoparticles under these test conditions. Although Au nanoparticles might be too expensive to be used in practical application for energy generation during wastewater treatment, the results of this study highlight the importance of the chemical properties and morphologies of the electrode surface on current generation. Such information might be valuable for the selection and development of anode materials for MFCs or MECs.

Microbial electrochemical cells might also provide an excellent platform for the study of bacteria–surface interactions since current, the result of the interactions, can be easily and accurately monitored. With recent developments in nanotechnology, we can decorate the anode surfaces with various nanomaterials to achieve well controlled surface properties, thus providing diverse electrode surfaces for the platform.

### 4. Conclusions

This study demonstrated that nano-decoration can greatly enhance the performance of microbial anodes. The anodes decorated with Au nanoparticles produced a current density of up to 20-fold higher than those of the plain graphite anodes. The anodes

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Fig. 6. Relationship between the maximum current densities and the area fraction (A) and particle counts (B) of Au (solid diamonds) and Pd (open circles) particles.
that decorated with Pd with similar morphologies, however, only produced 50–150% higher current than that of the control samples, indicating that the chemical composition of the nanoparticles affect the anodic performance significantly. Positive linear regression was obtained between the current densities and the Au particle size and negative correlation was obtained between the current density and the Au particle circularity, indicating that the size and shape of nanoparticles also affect the anodic performance.

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References


