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Enhanced electrical contact of microbes using Fe_3O_4/CNT nanocomposite anode in mediator-less microbial fuel cell

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ABSTRACT

A novel Fe_3O_4/CNT nanocomposite was synthesized and employed for the modification of carbon paper anode in a mediator-less microbial fuel cell (MFC) to enhance its performance. The Fe_3O_4/CNT composite modified anodes with various Fe_3O_4 contents were investigated to find the optimum ratio of the nanocomposite for the best MFC performance. The Fe_3O_4/CNT modified anodes produced much higher power densities than unmodified carbon anode and the 30 wt% Fe_3O_4/CNT modified anode exhibited a maximum power density of 830 mW/m^2. In the Fe_3O_4/CNT composite modified anode, Fe_3O_4 helps to attach the CNT on anode surface by its magnetic attraction and forms a multi layered network, whereas CNT offers a better nanostructure environment for bacterial growth and helps electron transfer from *E.coli* to electrode resulting in the increase in the current production with the catalytic activity of bacteria. The electrocatalytic behavior and all possible mechanism for their better performance are discussed in detail with the help of various structural and electrochemical techniques.

1. Introduction

Microbial fuel cell (MFC) is one of the promising green energy sources to produce electricity from organic wastes with the help of bacteria as catalyst. It converts the chemical energy in the organic wastes into electricity by bio-electrochemical reactions (Logan et al., 2006; Lovely, 2006).

The MFC comprises a bio-anode where the microorganisms disintegrate the organic wastes into small molecules while producing electrons and protons. Thus produced electrons transfer from the microbes to anode and further travel through the external circuit to the cathode where they are used to reduce the electron acceptors. Meanwhile, protons migrate through a proton exchange membrane (PEM) from the anode to the cathode and complete the circuit. This is the basic working mechanism of MFC, which results in the generation of electrical power as well as removal of organic waste simultaneously (Delaney et al., 1984; Roller et al., 1984). In spite of the promising merits of MFC, the power generated from the fuel cell is still low to limit its applications in energy generation industries.

The anode material is considered to be one of the key factors that influence the energy conversion in MFC along with cathodes and electrolytes. In the process of electricity generation from MFC, because the electron transfer from microbes to the anode is relatively slow process, the use of electron mediators is generally required for rapid electron transfer. Mediators such as 2-hydroxyl 1, 4-naphthoquinone (HNQ) or thionine have been generally used as electron shuttle to facilitate the electron transfer. These types of MFC are called mediated MFC where the mediators need to be replenished continuously to avoid toxicity and to reduce operational losses (Logan et al., 2006). Since Kim et al. demonstrated a possibility of mediatorless MFC with *Shewanella* species (Hyung Joo Kim et al., 2002), various metal reducing microorganisms such as *Geobacter and Shewanella* are reported to directly transfer electrons to the electrode in the electrocatalytic process of the mediatorless MFC (Chang et al., 2006; Zhang et al., 2006). These microbial organisms are known to effectively transfer electrons through nanowire without any mediators. The mediatorless MFC has provided stable power generation using various biomasses but has a low power output (Caccavo et al., 1994; You et al., 2006). The relatively low power density and poor energy conversion efficiency of the conventional MFC are resulted from sluggish electron transfer between bacteria and electrode. Modification of anode surface can reduce the charge transfer resistance and increase the electron transfer and there by improve the overall performance of MFC.

The modification of anode with various nano-engineering techniques has been proposed to be promising and efficient to facilitate the electron transfer between microbes and anode (Scott et al., 2007). Bacterial attachment and the formation of a biofilm or network on the anode surface are essential for the efficient biological transfer of electrons in an MFC. Various modification strategies

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including nanomaterials and fabrication methods have been developed so far to increase the electron-accepting ability of the electrodes and to improve electron transfer and power density. Qiao et al. (2007) investigated carbon nanotube/polyaniline nanostructure composite as anode materials and reported. They observed the highest electrochemical activity and maximum power density at 20 wt% CNT composite anode in *E.coli*-based MFC. A unique nanostructured polyaniline/mesoporous TiO_2 nanocomposite was also explored as an anode in *E.coli* MFC (Qiao et al., 2008), which reported that the best bio- and electrocatalytic performance was observed from the composite with 30 wt% PANI. Meanwhile, Feng et al. (2010) attained the maximum power density of 1303 mWm^{-2} from a polypyrrole/anthraquinone-2,6-disulphonic disodium salt (PPy/AQDS)-modified carbon felt anode, which is 13 times larger power than that obtained from the MFC equipped with unmodified carbon anode in the presence of Shewanella species. Interestingly, Sun et al. (2010) fabricated a CNT/TP modified anode with enhanced electron transfer and power production. Peng et al. (2012) also showed enhanced behavior of anode by rolling the mixture of Fe_3O_4 and activated carbon (AC) on anode surface with a maximum power density of 809 ± 5 mW/m^2. So, the anode surface structure and its ability to interact with bacteria are very important regardless of the electron transfer mechanism. Hence the modification of anode with nanomaterials is an efficient method to significantly enhance the generation of electricity in MFC.

With this background, in this work, we investigated a novel Fe_3O_4/CNT hybrid nanocomposite modified carbon anode in mediatorless MFC. Carbon nanotubes (CNTs) have been served as a promising option for electrode surface modification materials due to their unique mechanical and electrical properties. First we coated mono-dispersed Fe_3O_4 nanoparticles on CNT by using a solvothermal synthetic method. Then the prepared Fe_3O_4/CNT nanocomposite was introduced to *E.coli* culture medium to form a network of *E.coli* and Fe_3O_4/CNT nanocomposite. The multilayered network was coated on the carbon paper electrode by applying magnetic force and used as MFC anode. The Fe_3O_4/CNT anode with various Fe_3O_4 content is also investigated to find the optimum ratio of the nanocomposite. The enhanced electron transfer and increased MFC performance with different Fe_3O_4 (in Fe_3O_4/CNT anode) content is explained with the help of polarization curves and other electrochemical characterizations.

2. Materials and methods

2.1. Synthesis of Fe_3O_4/CNT

Fe_3O_4 was deposited on CNT using a solvothermal synthetic method reported detail in previous reports (Deng et al., 2012; Yoon et al., 2012). Stoichiometric amounts of Iron III acetylacetonate, $Fe(C_5H_8O_2)_3$ precursor were completely dissolved in triethylene glycol ($C_6H_{14}O_4$) (sigma Aldrich) with agitation. They were initially mixed with 0.1 g of CNT (JEO Co.) to form CNT suspended solutions. (The amounts of precursor used for preparing different ratios of Fe_3O_4 in Fe_3O_4/CNT are given in Table 1 in supplementary article). The prepared suspension was then reduced with triethylene glycol at 280 °C to form Fe_3O_4/CNT nanocomposite. The suspension was agitated uniformly throughout the reduction reaction using magnetic stirrer. Fe_3O_4/CNT nanocomposite with four different Fe_3O_4 compositions (viz. 10, 30, 50, and 80 wt%) were synthesized and studied in this work.

2.2. Microbe cultivation

A gram-negative bacterium *Escherichia coli* (*E.coli*) *K*12 of 2 μm size was used in this experiment and the aerobic culture was done in Luria–Bertani (LB) medium. The *E.coli K*12 colony in LB agar medium was extracted into a falcon tube containing 5 mL LB medium. Seed culture was carried out for 12 h at 160 rpm in a shaking incubator (37 °C). 1 mL of the seed culture medium was mixed with 20 mL of LB medium in a falcon tube followed by the main culture for 12 h at 160 rpm in a shaking incubator (37 °C) (Kim et al., 2002).

2.3. Assembly of anode

To prepare Fe_3O_4/CNT modified anode, 0.05 g of Fe_3O_4/CNT nanocomposite was introduced to *E.coli* culture medium in LB broth, vortexed for uniform dispersion of particles in the solution and then immobilized bacteria on Fe_3O_4/CNT nanocomposite by a culturing process for 2–3 h while continuously shaking at 160 rpm in a constant temperature incubator. This process allows the formation of a sort of network between *E.coli* and Fe_3O_4/CNT nanocomposite in the solution. An electrode of carbon paper (TGPH-090, Toray International Inc.) wrapped around a magnetic slit ($10 \times 10 \times 2$ mm^3) was placed in the same culture medium to form a multilayer of the *E.coli* and Fe_3O_4/CNT nanocomposite on the carbon paper electrode layer. In other words, a network of *E.coli* and Fe_3O_4/CNT nanocomposite is formed in a multilayered shape on the magnetic carbon electrode resulting in the formation of a conductive biocatalytic electrode. The conductive biocatalytic electrode was prepared with different Fe contents of Fe_3O_4/CNT nanocomposite (10, 30, 50 and 80 wt%) and fuel cell performance of the electrodes were comparatively investigated.

For a clear understanding the anode assembly is clearly shown in Fig. 1 in the supplementary article.

2.4. Fabrication and evaluation of MFC

The detailed MFC fabrication and MFC evaluation with its working conditions and details are explained in supplementary article.

2.5. Physical and electrochemical characterizations

The physical and electrochemical characterization details and techniques used to study them are also explained in the supplementary article.

3. Results and discussion

3.1. Structural characterizations

Crystallographic studies were performed on the synthesized metal/CNT composites with different Fe_3O_4 contents by using X-ray diffraction (XRD) spectroscopy. XRD spectra for the synthesized samples are shown in Fig. 1(a) as a function of contents. The characteristic (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) peaks appeared on the spectra are due to Fe_3O_4 [JCPDS 01-1111], whereas the (0 0 2) peak corresponds to CNT (Sun and Liu, 2005). This confirms that the deposited material on CNT in this work is Fe_3O_4. With increasing Fe_3O_4 content in Fe_3O_4/CNT, the intensity of the Fe_3O_4 related peaks increases, while that of CNT decreases, as shown in Fig. 1(b), suggesting the formation of well aligned Fe_3O_4 over CNTs.

The surface morphology of the synthesized Fe_3O_4/CNT nanocomposite was analyzed by TEM and FESEM measurements. The TEM images (Fig. 2(a)) clearly show the deposition of Fe_3O_4 nanoparticles over raw carbon nanotube surface and the density of the Fe_3O_4 nanoparticles increases with the increase of the Fe_3O_4 loading content. The diameter of CNT is seen to be 10–15 nm and