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Short Communication

Effects of surface charge, hydrophilicity and hydrophobicity on functional biocathode catalytic efficiency and community structure

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HIGHLIGHTS

- The hydrophilic −NH−NH_2 electrode showed a better nitrobenzene reduction efficiency.
- The hydrophobic −SH electrode showed a poorer nitrobenzene reduction efficiency.
- The hydrophilic electrode surface enriched more electroactive nitroaromatic reducers.
- Electrode surface characteristics could affect functional biocathodes performance.

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ABSTRACT

The bioelectrotransformation efficiency of various organic matters and corresponding electrode biofilm community formation as well as electron transfer efficiency in bioelectrochemical systems (BESs) with different modified electrodes has been extensively studied on the anode side. However, the effects of cathode interface characteristics towards the BESs bioelectrotransformation performance remain poorly understood. In this study, the nitrobenzene-reducing biocathode catalytic efficiency and community structure in response to different modified electrodes (control: hydrophobic and no charge; −SH: hydrophobic and single negative charge; −NH_2: hydrophilic and single positive charge −NH−NH_2: hydrophilic and double positive charges) were investigated. The biocathode transformation efficiency of nitrobenzene (NB) to aniline (AN) ($E_{NB\text{-}AN}$) was affected by the nature of electrode interface as well as the biocathode community formation and structure. Cathodes with hydrophilic surface and positive charges have performed well in the bioelectrotransformation experiments, and especially made an outstanding performance when inorganic $NaHCO_3$ was supplied as carbon source and cathode as the sole electron donor. Importantly, the hydrophilic surfaces with positive charges were dominated by the electroactive nitroaromatic reducers (*Enterococcus*, *Desulfovibrio* and *Klebsiella*) with the relative abundance as high as $72.20 \pm 1.87\%$ and $74.86 \pm 8.71\%$ for −NH_2 and −NH−NH_2 groups respectively. This could explain the higher $E_{NB\text{-}AN}$ in the hydrophilic groups than that of the hydrophobic −SH modified group. This study provides new insights into the effects of electrode interface characteristics on the BESs biocathode performance and offers some suggestions for the future design for the improvement of bio-electroremediation performance.

1. Introduction

Bioelectrochemical system (BES), a promising technology utilizing electrodes as the electron donor or acceptor to interact with electrochemical active bacteria (EAB), plays a critical role in the elimination of various environmental contaminants. As a result, in

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the past decade, various organic pollutants can be efficiently removed at both anode (e.g., total petroleum hydrocarbons, phenol, aniline, pyridine, benzene, and naphthalene) and cathode (e.g., nitroaromatics, azo dyes, reducible antibiotics, and halogenated aromatics and aliphatic hydrocarbons) of BESs (Liang et al., 2013, 2014; Cheng et al., 2015; Kong et al., 2015a, 2015b; Wang et al., 2015; Cui et al., 2017; Daghio et al., 2017; Jiang et al., 2018; Yun et al., 2018).

Undoubtedly, the efficient performance of BESs is highly dependent on the nature of electrode interface between the electrode and EAB. Therefore, the modification of the interfaces with biocompatible small molecules and nanomaterials, as an efficient approach to improve the performance of BESs, has aroused wide attention recently. The existing works mainly centered on altering the surface chemistry/morphology, and developing emerging materials and configuration (Guo et al., 2015). Overall, most studies are associated with the enhancement of functioning and electron transfer efficiency of anode as well as the microbial community formation (Yong et al., 2012, 2014; Guo et al., 2015; Wang et al., 2016; Sun et al., 2017). It is reported that positively charged and hydrophilic surfaces are more selective to electroactive microbes (e.g. *Geobacter*) and more conducive for anode biofilm formation (Guo et al., 2013). Moreover, the extracellular electron transfer (EET) is also improved on a hydrophilic electrode (Ding et al., 2015). A previous study also has found that positive-charge could enhance microbial electrosynthesis at the cathode, however, the modified cathode has changed the porosity simultaneously (Zhang et al., 2013). Nevertheless, there is little knowledge about whether the interface charge, hydrophilicity and hydrophobicity could affect the cathode biofilm community formation, structure and electrocatalytic efficiency without altering the electrode morphology.

In this study, cathodes with three kinds of modifications ($-NH_2$, $-NH-NH_2$, and $-SH$) were established to investigate the effects of interface charge, hydrophilicity and hydrophobicity on the functional biocathode catalytic efficiency and microbial community structure. Nitrobenzene (NB) was chosen as the model pollutant to explore the NB bioelectrotransformation efficiency. The objectives of this study were to (i) compare the difference of biocathode catalytic efficiency among the functional biofilms formed on different modified cathode surfaces and (ii) answer the question that whether the interface charge, hydrophilicity and hydrophobicity would affect the cathode biofilm community formation, structure and electrocatalytic efficiency. The current study offers new insights into the effects of electrode interface characteristics on the BESs biocathode performance and provides some suggestions on the design of electrode interface characteristics for the enhanced bioelectroremediation in the future.

2. Materials and methods

2.1. Chemicals

NB (>98% purity) and AN (>98% purity) was purchased from Aladdin (Shanghai, China). HPLC grade methanol was purchased from Sigma-Aldrich (St. Louis, Mo, USA). Three coupling agents (USi-1301 (γ-Aminopropyltrimethoxysilane), USi-D1301 (N-β-(Aminoethyl)-γ-aminopropyltrimethoxysilane), and USi-5301 (γ-Mercaptopropyltrimethoxysilane) were used in the experiment. Coupling agents related to electrode modification were purchased from Nanjing Union Silicon Chemical Co., Ltd (Nanjing, China). Other chemicals were at least of analytical grade.

2.2. Electrode preparation and modification

The carbon cloths (CC) (3 cm in diameter) were used as cathodes, pretreated by immersing in acetone and sonicating for 1.5 h. As soon as standing for 2.5 h, the CC electrodes were thoroughly rinsed by sonicating in Milli-Q water and anhydrous alcohol twice, and once for 0.5 h respectively. After hermetically immersing in nitric acid for 12 h, the CC electrode surface activations were finished, and repeated the rinsing process. Functional groups were attached to the CC electrodes via coupling agents that contained $-NH_2$, $-NH-NH_2$ and $-SH$ (Fig. 1a). The modification was followed by dipping the CC electrodes into a solution of coupling agents dissolved in anhydrous alcohol for 2 h at room temperature. This process provided sufficient time for the alkoxy group (-Si-O-) in the coupling agents to react with the hydroxyl on the CC surfaces, and formed covalent forces between them which was strong enough and hard to break. After reaction, the electrodes were rinsed with Milli-Q water to remove the residua and dried. Non-modified CC electrode was set as a control group.

2.3. Reactor construction and cathode biofilm establishment

The dual-chamber BES reactor was constructed as reported previously (Kong et al., 2015a). Pretreated carbon brushes (4 cm in diameter by 3 cm in length, TOHO TENAX CO., Ltd., Tokyo, Japan) were used as anode (Kong et al., 2015a). The modified CC served as the cathodes (include a control group), and was pierced with titanium wire (1 mm in diameter, Baoji LiXing Titanium Group Co., Ltd., China) as current collector. A saturated calomel electrode (SCE, 0.247 V vs standard hydrogen electrode (SHE), model-217, Shanghai

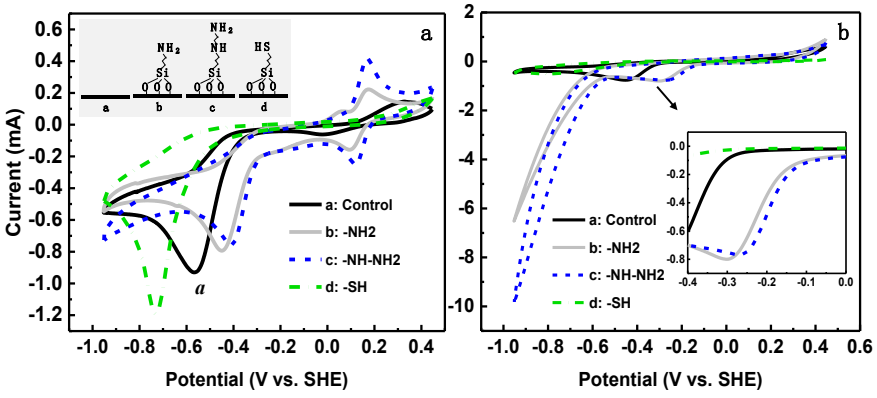

Fig. 1. Cycle voltammograms of modified (a) abiotic cathodes and (b) biocathodes.