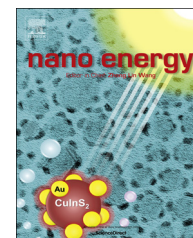




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RAPID COMMUNICATION

Regulating the respiration of microbe: A bio-inspired high performance microbial supercapacitor with graphene based electrodes and its kinetic features



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3D graphene scaffold;
Single-layer graphene film

Abstract

Toward a carbon neutral renewable energy conversion and storage device, we present a novel bio-inspired microbial supercapacitor, utilizing unique pseudocapacitance formed by exoelectrogen, a specific species of bacteria named *Geobacter spp.* grown on single-layer graphene film and 3D graphene-scaffold electrodes. Charging and discharging the microbial supercapacitor were performed by regulating the respiration of the exoelectrogen. Substantially high maximum current and power densities, 531.2 A/m² (1,060,000 A/m³) and 197.5 W/m² (395,000 W/m³), respectively, are marked. The microbial supercapacitor demonstrates high cycle stability of over 1 million. A specific capacitance of 17.85 ± 0.91 mF/cm² is demonstrated, which is 4.4 fold to 2 orders of magnitude higher than previously reported supercapacitors having graphene-based electrodes, suggesting a promising alternative energy storage device. Furthermore, the microbial supercapacitor was used to deduce quantitative kinetic parameters of extracellular electron transfer (EET) by fitting discharging curves of the supercapacitor, which is critical to fully understand the EET of *Geobacter spp.* and determining the rate-limiting mechanism. At the initial-stage biofilm, the acetate turnover is the slowest among individual EET steps, whereas for fully-grown stage biofilm, kinetics of both acetate turnover and electron transfer from inside exoelectrogen to extracellular redox cofactors are rate-limiting. Our

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results also suggest *cytochrome c* may not be the main electron storage units of a microbial supercapacitor, regardless of initial- or fully-grown stage biofilms.
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Introduction

Supercapacitors, or electrochemical capacitors, are attractive due to their high current and power densities, low maintenance, and high shelf and cycle lifetime [1,2]. Most supercapacitors deploy materials of either high specific area, such as activated carbon, carbon nanotubes, and graphene; others utilize pseudo-capacitive materials, such as metal oxides (RuO_2 , and MnO_2) [3]. Inspired by the recent remarkable surge of bio-inspired materials research [4–7], biological pseudocapacitance, which includes redox cofactors inside biological entities, might be promising energy storage materials, due to its abundance, renewability and environmental friendliness, to replace conventional redox-based pseudocapacitance made from non-renewable compounds [8]. However, biological pseudocapacitance often fails to transfer electrons between biological entities and electrodes because the outer membranes of cells prohibit the exchange of electrons between redox cofactors inside the cells and the electrodes. One exception to this is specific species of bacteria used in microbial electrochemical technologies, named exoelectrogens. Their unique capability allows transferring electrons outside their bodies to electrodes to complete their respiration process, named extracellular electron transfer (EET). Exoelectrogens have been implemented in various microbial electrochemical technologies (METs), such as microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial reverse electrodialysis cells (MRCs), etc. [9–14]. Recently, several reports demonstrated that exoelectrogens, such as *Geobacter*, *Shewanella*, and *Proteobacteria*, store electrons, which could be used as capacitors [15–22], having current density in the range of $1.2\text{--}90\text{ A/m}^2$. The high current density observed in these reports demonstrated the ability to use biological pseudocapacitance as a potential carbon-neutral and renewable method for energy generation and storage.

In this work, we present a novel high performance microbial supercapacitor with both single-layer graphene and 3D graphene scaffold anodes which can store and release electrons produced by the metabolism of *Geobacter* spp. The charging and discharging characteristics of microbial supercapacitor allow us to study the kinetics of electron transfer without significant damage to biofilm. By fitting a kinetics model to the discharging current profiles at initial-stage and fully-grown biofilms, the microbial supercapacitor offers quantitative measurements of kinetics parameters, which are critical for understanding EET of exoelectrogens.

Results and discussions

A schematic of the exoelectrogen, *Geobacter* spp., grown on both single-layer graphene and 3D graphene scaffold is shown in Figure 1(a) and (b) (not drawn to scale for visual

illustration). A high speed switch was implemented to characterize a microbial supercapacitor, as shown in Figure 1(c). When the switch is off, *Geobacter* are unable to complete their respiration process, resulting in storage of electrons in redox cofactors (charging step) (Figure 1(d)). When the switch is on, electrons stored inside redox cofactors are transferred to the anode, and then get oxidized at the cathode by oxidizers (discharging step) (Figure 1(e)).

A single-layer graphene film prepared by chemical vapor deposition (CVD) on a thin film gold (Figure S1) was used as a current collector due to its high conductivity and excellent electrochemical characteristics [23]. The sheet resistance of single-layer graphene film on the thin film gold was measured at $4.13\ \Omega/\text{square}$. A 3D graphene scaffold prepared by CVD was also implemented due to its higher specific area and lower sheet resistance (Figure S1). The specific surface area of 3D graphene is $850\text{ m}^2\text{ g}^{-1}$ [24], which is comparable with those of activated carbon reported by Alvarez-Gallego et al. 2012 ($299\text{--}745\text{ m}^2\text{ g}^{-1}$) [25] and Zhang et al. 2014 ($267\text{--}922\text{ m}^2\text{ g}^{-1}$) [26]. The sheet resistance of 3D graphene scaffold was measured at $0.335\ \Omega/\text{square}$. Morphology and thickness of biofilm grown on the single-layer graphene was imaged with optical interference microscopy (Figure 1(f)). The thickness of biofilm islands was between $20\ \mu\text{m}$ and $80\ \mu\text{m}$. A scanning electron microscope (SEM) image of biofilm shows rod-shaped microorganisms (Figure 1(f) inset), commonly found in the biofilm of MFCs [27–29]. Morphology of biofilm grown on the 3D graphene scaffold was visualized using SEM, and dense biofilm grew on the graphene scaffold (Figure 1(g)). 16 S rRNA gene pyrosequencing identified the most predominant family *Geobacteraceae* accounting for 87.5% of total 9813 sequences. The neighbor-joining phylogenetic tree showed that the majority of OTU 1560 in the family *Geobacteraceae* had 98.9% similarity to uncultured *Geobacter* (JQ724345), and *Geobacter sulfurreducens* (NR075009, 97.9% sequences similarity) (Figure 1(h) and (i)). This result shows that *Geobacter* spp. are the major exoelectrogen in the biofilm.

Figure 2(a) shows the cyclic voltammetry (CV) curve of the supercapacitor with single-layer graphene film and 3D graphene scaffold, respectively, at scan rate of 100 mV/s . Pseudocapacitance was observed by the redox peaks in the CV curve. It is obvious that the biofilm on the 3D scaffold electrode demonstrates a significantly higher pseudocapacitance, due to the high specific surface area. Figure 2(b) shows CV diagram at a scan rate of 10 mV/s for the supercapacitor with single-layer graphene film. This CV diagram is a sigmoidal curve commonly found in biofilm having *Geobacter sulfurreducens* or *Geobacter*-enriched culture [29–31], supporting the bacterial community analysis. The sigmoidal curve can be represented with Nernst-Monod equation. The maximum current was 0.58 mA in the

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