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Regular Article

Self-assembly of an electronically conductive network through microporous scaffolds

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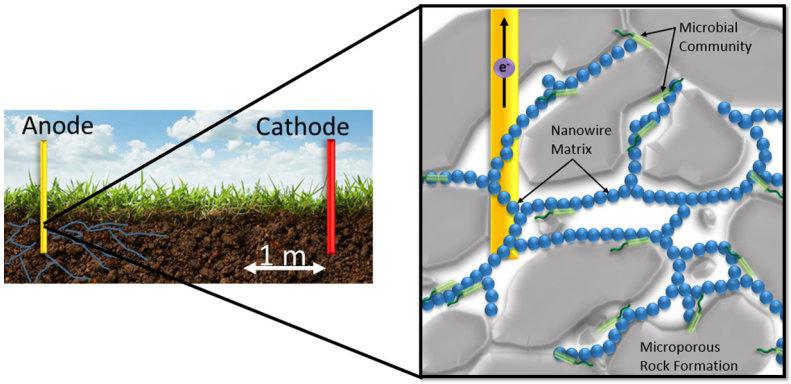
GRAPHICAL ABSTRACT



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ABSTRACT

Electron transfer spanning significant distances through a microporous structure was established via the self-assembly of an electronically conductive iridium oxide nanowire matrix enveloping the pore walls. Microporous formations were simulated using two scaffold materials of varying physical and chemical properties; paraffin wax beads, and agar gel. Following infiltration into the micropores, iridium nanoparticles self-assembled at the pore wall/ethanol interface. Subsequently, cyclic voltammetry was employed to electrochemically crosslink the metal, erecting an interconnected, and electronically conductive metal oxide nanowire matrix. Electrochemical and spectral characterization techniques confirmed the formation of oxide nanowire matrices encompassing lengths of at least 1.6 mm, 400× distances previously achieved using iridium nanoparticles. Nanowire matrices were engaged as biofuel cell anodes, where electrons were donated to the nanowires by a glucose oxidizing enzyme.

1. Introduction

Biomimicry attempts to emulate nature's strategies in order to fabricate solutions to every day issues. Several energy related technologies are similar to systems found in nature including solar cells, fuel cells, and batteries. Each of these examples employ the transport of electrons, or the flow of current, which is harnessed to do work. However, many of these technologies are hindered by poor electronic conductivity and slow electron transfer kinetics on the nanoscale.

It is well known that rates of electron transfer are inversely proportional to the distance between the electron donor and the acceptor [1,2]. Typically, for a single donor-acceptor pair, rapid

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electron transfer occurs over extremely small distances (ca. 1.0 Å). When considering energy-related technologies, however, a significantly longer electron transfer distance is vital. In the relevant scientific literature, the term "long-distance electron transfer" is very broad, and can include multiple acceptor and donor sites. In nature, there are numerous recognized examples of long-distance electron transfer spanning from tens of angstroms [1] to kilometers [3].

Over millions of years, nature has developed and evolved intricate methods in which to propagate life. Arguably, the core component to life is the ability of organisms to transport energy. Photosynthesis is a well-documented example of long-distance intracellular electron transfer [4,5], where, electron transfer of up to 17 Å has been recorded [6]. In comparison, some microbial species are capable of direct, intercellular electron transfer spanning over distances of up to 1 cm across multiple cells, [7] and multiple microbial species [8–10]. Geobacters [11–14], Shewanella [15,16], some photosynthetic cyanobacteria [16], and Desulfobulbaceae [7,17] – for example – produce electronic conductive nanowires which establish electron transport between individual microbes, and bridge non-conductive gaps to extracellular electron acceptors, such as insoluble metal oxides [13,16,18].

The concept of "geobatteries" has been documented since the 1990s, where electrons are transferred over several kilometers through geological formations [3,19,20]. These "self-potential anomalies" are associated with an interconnected network of highly conductive graphitic layers present at the mineral surface of ore deposits, located at steeply inclined fault zones [21]. Magnitudes of up to 1 V have been recorded. More recently, "biogeobatteries" [22,23] have been discovered, where spatially separated redox reactions are coupled by microbial communities interconnected with semiconductor minerals. Redox gradients span millimeter to meter [3] to kilometer [24] length scales and can generate >100 mV [22].

Engineers have thus far, been largely unsuccessful at replicating the long-distance electron transfer exhibited by nature, using nanoscale materials. Biomimicry, however, may provide the insight necessary to enhance already realized biologically-inspired devices, such as biofuel cells or biobatteries. For example, the development of anode materials that can span several meters through a microporous formation (such as dirt or rock) would permit electron transfer between microbes and fuel molecules that may otherwise be challenging to reach. Such an understanding could further the development of *in situ* devices, as well as aid in environmental reclamation.

The said ability of specific microbes to assemble electronically conductive pili between cells and electrodes has already been exploited for the fabrication of biofuel cells [25] and for biofuel fabrication [26]. Electronically conductive nanowires could be emulated using metal or polymeric materials, thereby providing a connection between otherwise non-electronically conductive microbial communities, introducing new fuel sources. Additionally, numerous species of microbes flourish in high surface area, porous media (such as rock or sediment), and as such, these engineered pili will provide an avenue for electron transfer into confined pore environments [16].

Electronically conductive nanowires (NWs), and electron transfer matrices have been engineered from a variety of materials. The most common include carbon nanotubes [27,28], TiO_2 (500 nm–7 μm) [29] and silicon [30] nanowires, which have been used as electron transport pathways for photovoltaic cells. Cu [31] and ZnO [32] nanowires are used for optoelectronics, and various other metal nanowires, including, Pd [33], Au [34], Ag [35], Pt [36] and Ir [37,38], have been used for sensing applications. Iridium, in particular, has been studied extensively for its use as an electron transfer matrix for glucose sensing [38,37], show-casing its ability to accept electrons from biological materials. In this instance, electron transfer was achieved over distances of up to 4 μm [38,37]. In comparison, a Pd nanowire array was fabricated by Slaughter and Kulkarni, where electron transfer was achieved over distances of 98 μm [33].

A downside to using pre-fabricated nanowires (as opposed to generating them *in situ*), is that, it is difficult to inject the NWs into confined microporous environments, and subsequently interconnect them for rapid electron transfer kinetics. Consequently, an innovative method to readily self-assemble nanoparticles (NPs) into nanowires *in situ* is realized. To simulate porous formations, two model scaffolds with tunable pore size and lengths, hydrophobicities, structural integrities, and particle sizes were designed; paraffin wax beads, and 2 wt.% agar gel. Micron-sized paraffin beads have been utilized as porogens for tissue engineering, as they allow for good porosity and pore size control [39–41]. It is anticipated that, the NPs (injected as a sol) are driven to the liquid/paraffin interface, where they self-organize, fulfilling the need to decrease their surface energies. Agar/agarose gels have also previously been employed in the literature as templates for fabricating various macroporous structures [42–45]. It is hypothesized that, the oxygen groups on the agar polymer interact with the NPs, drawing them to the walls of the pores. To secure and interconnect the NPs to form a conductive NW matrix within both structures, the NPs are electrochemically crosslinked.

Interconnected IrOx nanowire (NW) matrices were successfully engineered throughout both the agar and paraffin bead scaffolds, via a self-assembly process. This technique allowed for the unique ability to transfer electrons over extended distances through microporous media, where, electron transfer would otherwise be challenging. Electron transfer between enzymes and the intercon-

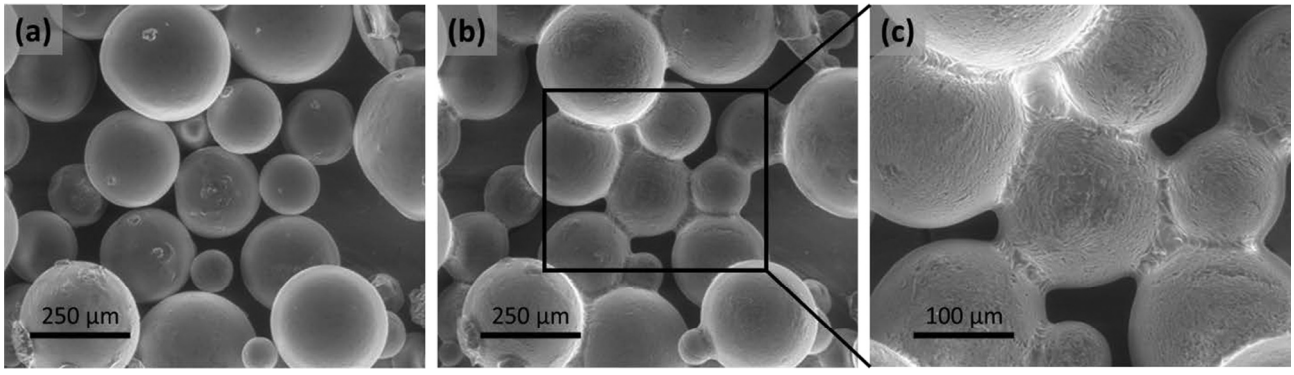

Fig. 1. Environmental scanning electron microscopy images showing naked paraffin beads (<300 μm dia.). (a) Beads prior to sintering and (b) beads after sintering at 55 °C, and (c) a higher magnification image of (b). Images were taken at 100 Pa H_2O vapor.