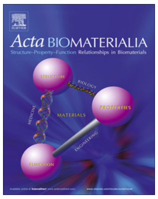
ARTICLE IN PRESS

Acta Biomaterialia xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat



Review article

Microbial nanowires – Electron transport and the role of synthetic analogues

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ARTICLE INFO

Article history:
Received 23 August 2017
Received in revised form 7 January 2018
Accepted 9 January 2018
Available online xxxx

Keywords:
Conducting nanowires
Electron transfer
Peptide assembly
Bioelectronics

ABSTRACT

Electron transfer is central to cellular life, from photosynthesis to respiration. In the case of anaerobic respiration, some microbes have extracellular appendages that can be utilised to transport electrons over great distances. Two model organisms heavily studied in this arena are *Shewanella oneidensis* and *Geobacter sulfurreducens*. There is some debate over how, in particular, the *Geobacter sulfurreducens* nanowires (formed from pilin nanofilaments) are capable of achieving the impressive feats of natural conductivity that they display. In this article, we outline the mechanisms of electron transfer through delocalised electron transport, quantum tunnelling, and hopping as they pertain to biomaterials. These are described along with existing examples of the different types of conductivity observed in natural systems such as DNA and proteins in order to provide context for understanding the complexities involved in studying the electron transport properties of these unique nanowires. We then introduce some synthetic analogues, made using peptides, which may assist in resolving this debate. Microbial nanowires and the synthetic analogues thereof are of particular interest, not just for biogeochemistry, but also for the exciting potential bioelectronic and clinical applications as covered in the final section of the review.

Statement of Significance

Some microbes have extracellular appendages that transport electrons over vast distances in order to respire, such as the dissimilatory metal-reducing bacteria *Geobacter sulfurreducens*. There is significant debate over how *G. sulfurreducens* nanowires are capable of achieving the impressive feats of natural conductivity that they display: This mechanism is a fundamental scientific challenge, with important environmental and technological implications.
Through outlining the techniques and outcomes of investigations into the mechanisms of such protein-based nanofibrils, we provide a platform for the general study of the electronic properties of biomaterials. The implications are broad-reaching, with fundamental investigations into electron transfer processes in natural and biomimetic materials underway. From these studies, applications in the medical, energy, and IT industries can be developed utilising bioelectronics.

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https://doi.org/10.1016/j.actbio.2018.01.007

Please cite this article in press as: R.C.G. Creasey et al., Microbial nanowires – Electron transport and the role of synthetic analogues, Acta Biomater. (2018), https://doi.org/10.1016/j.actbio.2018.01.007

1. Electron transfer and its central role in supporting cellular life

At the heart of all metabolic processes is electron transfer. In the mitochondria of higher animals and plants cells (eukaryotes), electron transfer takes place as a cascade of sequential electronic reactions through which low-redox-potential electron donors, such as nicotinamide adenine dinucleotide hydride (NADH), donate electrons to a series of redox cofactors associated with the cell membrane. These cofactors then either bind to protein complexes or remain freely-diffusing within the phospholipid layer. At the end of this reaction chain, oxygen, as a high-redox-potential electron acceptor, is reduced [1]. This process releases energy as the result of the formation of a *trans*-membrane proton electrochemical gradient (*proton motive force*, Δp), which is used for the production of ATP, the energy currency of life.

By contrast, respiration in prokaryotes can occur in the absence of oxygen using a diverse range of soluble and insoluble electron acceptors. Some species are capable of respiring using elemental sulphur and sulphur oxyanions [2], organic sulphoxides and sulphonates [3,4], organic N-oxides [5,6], nitrogen oxyanions and nitrogen oxides [7], halogenated organics [8–10], transition metals such as Fe(III) and Mn(IV) [11], metalloid oxyanions such as selenate and arsenate [12–14], and radionuclides such as U(VI) [15,16] and Tc(VII) [17]. Because of this flexibility, prokaryotes have been able to inhabit some of the most extreme regions on Earth and have a remarkable ability to thrive under conditions with limited availability of a terminal electron acceptor [18].

Bacteria belonging to the genus *Shewanella* and *Geobacter* are particularly well-studied examples of dissimilatory metal-reducing bacteria (DMRB), known to be capable of reducing insoluble metal oxides and other extracellular electron acceptors in the solid form (including electrodes), by means of extracellular electron transfer (EET) [19,20]. Since the cellular (cytoplasmic) membrane is an efficient electrical insulator and a physical barrier, these microorganisms have developed resourceful mechanisms to achieve EET. For example, *Shewanella oneidensis* MR-1 uses the metal reducing (Mtr) pathway, which includes a series of protein components (i.e., CymA, MtrA, MtrB, MtrC, and OmcA) to electrically link the *quinone* and *quinol* pool in the cytoplasmic membrane with the outer membrane to the surface of Fe-containing minerals [21]. *Geobacter sulfurreducens* PCA, on the other hand, it is proposed that it uses a *trans*-outer membrane porin-cytochrome complex containing OmcB and a porin-like outer membrane protein along with a periplasmic *c*-type cytochrome to transfer electrons across the outer membrane [22]. In addition, long-range electron transfer to distal minerals or other cells can be achieved by *G. sulfurreducens* PCA using pilin nanofilaments (known as *bacterial nanowires*) [23], possessing electronic conductivities comparable to that of conducting polymer nanowires [24,25]. In fact, the microbial nanowires of several strains of *G. sulfurreducens* have been shown to be conductive *in vivo* over a long-range (50 μm or more when assembled to form biofilms) [26]. Other examples of long-range electron transfer exist in nature. For instance, the cable bacteria *Desulfobulbaceae*, found in marine sediments, forms long multicellular filamentous structures whereby the transport of electrons occurs at the centimetre scale [27].

Understanding the way in which protein-based nanowires conduct electrons over such long distances has important scientific and technological implications [28,29]. In addition, the respiration of these microorganisms plays a major role in global biogeochemical cycles of nutrients. Their unique metabolism can be exploited in a variety of seminal technologies based on microbial bioelectrochemistry with applications that include bioremediation, biocorrosion control, energy generation from the treatment of waste in microbial fuel cells [30], to name a few. Furthermore, protein-based nanowires represent an exciting technological opportunity in biosensors and other bioelectronics applications [31,32]. In this review, we will discuss the fundamental mechanisms of electron transfer relevant to biomolecules, followed by an exploration of the current contrasting hypotheses for the mechanisms of extracellular conductivity in model prokaryotic organisms. To stimulate further work in this area, we have outlined some strategies for clarifying the mechanism of electron transport in *Geobacter* nanowires

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