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Solar biosupercapacitor

Elena González-Arribas [a,1], Olga Aleksejeva [a,1], Tim Bobrowski [b], Miguel Duarte Toscano [c], Lo Gorton [d], Wolfgang Schuhmann [b], Sergey Shleev [a,*]

[a] Biomedical Science; Faculty of Health and Society, Malmö University, Jan Waldenströms gata 25, 21428 Malmö, Sweden
[b] Analytical Chemistry – Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany
[c] Novozymes A/S, Krogshoejvej 36, 2880 Bagsvaerd, Denmark
[d] Department of Biochemistry and Structural Biology, Lund University, P.O. Box 124, 22100 Lund, Sweden

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ABSTRACT

Here we report on an entirely new kind of bioelectronic device – a solar biosupercapacitor, which is built from a dual-feature photobioanode combined with a double-function enzymatic cathode. The self-charging biodevice, based on transparent nanostructured indium tin oxide electrodes modified with biological catalysts, *i.e.* thylakoid membranes and bilirubin oxidase, is able to capacitively store electricity produced by direct conversion of radiant energy into electric energy. When self-charged during 10 min, using ambient light only, the biosupercapacitor provided a maximum of 6 mW m^{-2} at 0.20 V.

1. Introduction

Identifying economical, technically undemanding electric power sources, relying on renewable catalysts, is a major scientific and technological challenge. Among many possible catalyst candidates, biological catalysts, in the form of redox enzymes, organelles, and living cells, are highly active and renewable. Also, biological catalysts can be produced at low cost, if sufficiently high production volumes are considered.

Electric power can be generated by the transformation of other energy forms into electric energy. On a global scale, the dominant source of energy is electromagnetic radiation, *i.e.* radiant energy. Thus, life on our planet relies almost exclusively on sunlight, and solar energy accumulated by living organisms in the past is currently converted to electrical energy by the burning of fossil fuels. In terms of the energy flow from the sun, less than about 0.02% of the total solar energy reaching the surface of the Earth, *i.e.* $3.8 \cdot 10^{24}$ J over a year, would satisfy the present yearly global energy demands ($5.6 \cdot 10^{20}$ J) [1]. Given this vast supply of renewable energy, biological solar cells (bio-solar cells), *i.e.* devices based on biocatalysts, which can directly transform solar energy into electric energy, are in extreme scientific focus nowadays [2–4]. Extensive research on the use of various photosynthetic elements including photosynthetic reaction centers (bacterial, photosystem I and photosystem II) has generated different mediator-based photobioelectrodes [5–9]. For real practical applications, among many different requirements, devices should be simple to construct and non-toxic, and mediator-less bio-solar cells fully satisfy these criteria.

Bio-solar cells consisting of a mediator-less thylakoid bioanode, and either a platinum air-breathing cathode [10,11] or a laccase based biocathode [12–14], were reported earlier. Nanostructured materials, such as carbon quantum dots incorporated into a thylakoid suspension [15], or thylakoids tethered to supports modified with multi-walled carbon nanotubes [14], were used to increase the number of biological species in contact with the carbonaceous surface, thus providing a larger surface area for mediator-less bioelectrocatalysis and improve the photocurrent generation. The modification of thylakoid bioanodes with membrane-intercalating conjugated oligoelectrolytes tentatively enhance the contact between biological species and the electrode, resulting in a 1.4-fold increase of photocurrent densities in amperometric experiments, and also higher power output of the bio-solar cell [16].

However, all previously disclosed mediator-less bio-solar cells were opaque, and photocurrents were generated using powerful focused artificial light sources, with limited bearing on real practical applications. Moreover, closed systems have not been used for this type of devices and, a single compartment bio-solar cell, incorporating a mediator-less thylakoid anode and a bilirubin oxidase cathode, has not been reported so far. Here we show a miniature transparent bio-solar cell able to generate electricity using only ambient daylight. In the biodevice, the thylakoid membrane modified anode and bilirubin oxidase modified cathode, are ionically coupled in a closed system at neutral pH (Fig.

* Corresponding author.
E-mail address: sergey.shleev@mah.se (S. Shleev).
[1] E. González-Arribas and Olga Aleksejeva equally contributed to the present work.

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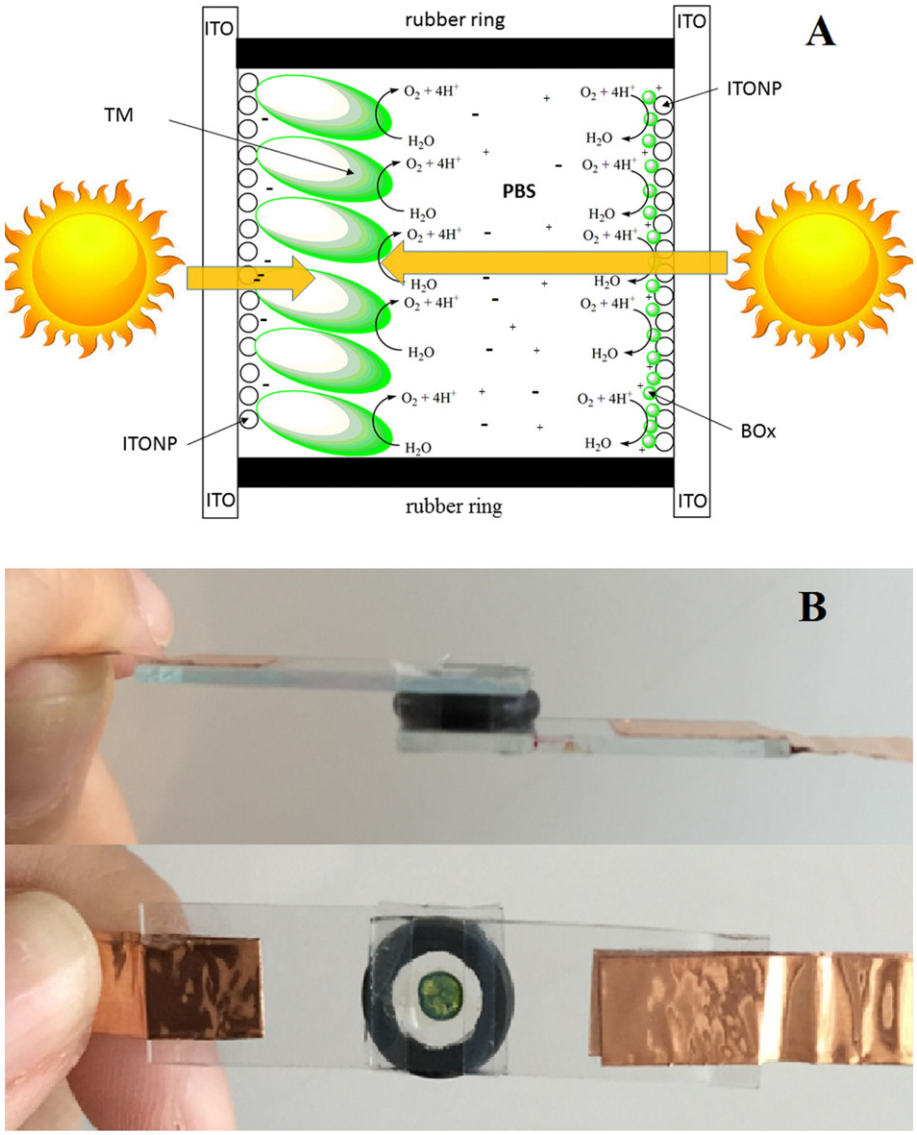

Fig. 1. Solar biosupercapacitor. (A) Molecular mechanism of function of solar biosupercapacitor. ITO – indium tin oxide coated rectangular glass slide, ITONP – indium tin oxide nanoparticle, TM – thylakoid membrane, BOx – bilirubin oxidase. (B) Images of a transparent mediator-less solar biosupercapacitor.

1A). However, owing to the mediator-less design, only small photocurrents were registered. One possibility to improve the power output is to store solar energy, and operate the biodevice in pulse mode, rather than in continuous mode.

Photosynthetic living organisms, *e.g.* green plants, algae and cyanobacteria, store solar energy in chemical bonds, forming molecular oxygen (O_2) and energy-rich carbohydrates from water and carbon dioxide. Biological solar cells, as well as conventional solar cells based on abiotic materials, directly convert solar energy into electric energy and are not *per se* designed to store the electricity generated. Thus, external electric energy storing devices, such as capacitors and/or rechargeable batteries, are required, which in the end increase not only the monetary but also the environmental costs of electric energy. Thus, a hybrid device, in which electromagnetic energy is directly converted into electric energy, which is concurrently stored within the appliance used for conversion, would attenuate the complexity, minimize losses, and reduce both cost aspects.

Very recently hybrid devices based on chemical energy were constructed and tested, *i.e.* "charge-storing fuel cells", or, in other words, "self-charging chemical supercapacitors" [17]. In these hybrid devices [18], including biodevices [19–21], chemical energy is directly converted into electric energy, which is capacitively stored within a singular contrivance. Below we detail the very first solar biosupercapacitor, which is built from transparent and nanostructured, *i.e.* highly capacitive, indium tin oxide (ITO) electrodes. The biodevice is able to convert solar energy directly into electric energy, which is capacitively stored within the device. Because of the materials used, the resulting biodevice is a simple to build, inexpensive, and sustainable electric power source for low-power low-voltage electronics.

2. Experimental

2.1. Chemicals and materials

$Na_2HPO_4 \cdot 2H_2O$, KH_2PO_4, NaCl, KCl, $MgCl_2$ were purchased from Sigma-Aldrich (St. Louis, USA). Tris(hydroxymethyl)aminomethane was obtained from Kebo AB (Stockholm, Sweden). Glycine was obtained from Fisher Chemical (Leics, United Kingdom). Sucrose was purchased from BDH Laboratory supplies (Poole, England). 100% methanol was obtained from VWR Chemicals (Paris, France) and 99.5% ethanol from CCS Healthcare AB (Malmö, Sweden). Argon (Ar) and O_2 were supplied by AGA Gas AB (Sundbyberg, Sweden). All chemicals were of analytical grade and used without further purification. All solutions were prepared using water purified with the PURELAB