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Scalable long-term extraction of photosynthetic electrons by simple sandwiching of nanoelectrode array with densely-packed algal cell film

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ABSTRACT

Direct extraction of photosynthetic electrons from the whole photosynthetic cells such as plant cells or algal cells can be highly efficient and sustainable compared to other approaches based on isolated photosynthetic apparatus such as photosystems I, II, and thylakoid membranes. However, insertion of nanoelectrodes (NEs) into individual cells are time-consuming and unsuitable for scale-up processes. We propose simple and efficient insertion of massively-populated NEs into cell films in which algal cells are densely packed in a monolayer. After stacking the cell film over an NE array, gentle pressing of the stack allows a large number of NEs to be inserted into the cells in the cell film. The NE array was fabricated by metal-assisted chemical etching (MAC-etching) followed by additional steps of wet oxidation and oxide etching. The cell film was prepared by mixing highly concentrated algal cells with alginate hydrogel. Photosynthetic currents of up to 106 nA/cm^2 was achieved without aid of mediators, and the photosynthetic function was maintained for 6 days after NE array insertion into algal cells.

1. Introduction

Photosynthesis is a highly efficient energy conversion process which occurs in nature. In photosynthesis, plants convert solar energy into electrons, photosynthetic electrons (PEs), and store a portion of the PEs in a form of carbohydrates with the quantum efficiency close to 100% (Wraight and Clayton, 1974). Thus, there have been many attempts to develop bio-solar energy harvesters that extract usable electrical energy from the photosynthesis without any environmental sacrifice unlike most commercially-available photovoltaic solar cells.

PEs can be extracted from isolated photosynthetic apparatus such as thylakoid membranes (Calkins et al., 2013; Hamidi et al., 2015; Hasan et al., 2014; Kavadiya et al., 2016; Kirchhofer et al., 2015; Rasmussen and Minteer, 2014; Sekar et al., 2016), photosystem I (PS I)(Ashraf et al., 2017; Beam et al., 2015; Ciesielski et al., 2008; Gizzie et al., 2015a, 2015b; Hasan et al., 2015; LeBlanc et al., 2014; Mershin et al., 2012; Robinson et al., 2017a; Robinson et al., 2017b; Tapia et al., 2017; Yang et al., 2016) or photosystem II (PS II)(Cai et al., 2015; Feng et al., 2015; Hasan et al., 2015, 2017; Li et al., 2016; Maly et al., 2005; Miyachi et al., 2017; Tahara et al., 2016; Terasaki et al., 2008; Tsargorodska et al., 2016; Yehezkeli et al., 2012, 2013). Using the photosynthetic apparatus, photocurrent density of up to ~ 362 μA/cm^2 was achieved (Mershin et al., 2012). However, since the isolated apparatus are less stable compared to when they are within the whole cells, the PE currents decrease rapidly (Gorby et al., 2006; Reguera et al., 2005).

As another approach, nanoelectrodes (NEs) can be inserted into living photosynthetic cells and PEs can be directly extracted from the inserted cells (Hong et al., 2017; Kim et al., 2016; Ryu et al., 2010). Such PE extraction by NE insertion into the whole cell is highly sustainable and PE extraction for 7 days was previously demonstrated (Hong et al., 2017). When a NE had a small enough diameter, algal cells inserted by the NE maintained their normal functions including cell division and proliferation. However, the NE insertion was performed for single cells, from which PE currents of about 1 pA or less was extracted. To collect more PEs in this NE insertion approach, an array of vertically-aligned NEs was developed for insertion of NEs into multiple algal cells (Kim et al., 2016). Algal cells were sequentially inserted by NEs and the corresponding increase of PE currents was observed. Although this NE array system demonstrated the possibility of enhanced PE collection from multiple cells, NE insertion into cells was still limited as a manual process that was time-consuming and unsuitable for further scale-up.

In this study, we propose simple and efficient insertion of massively-populated NEs into cell films in which algal cells are densely packed in a monolayer (Fig. 1). After stacking a cell film over an NE array, gentle

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