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Fabrication of scalable and flexible bio-photoanodes by electrospraying thylakoid/graphene oxide composites

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ABSTRACT

For extraction of photosynthetic electrons (PEs) from plant cells and algal cells, there have been many approaches using living algal cells or isolated photosynthetic apparatus such as photosystem II, photosystem I, and thylakoid membranes (TMs). Among these, bio-photoanodes coated with TMs demonstrated stable performance and the possibility for their practical applications. When a TM photoanode is prepared, TMs are deposited on the surface of a metal electrode. However, since the thickness of TM films determines the light absorption and electron transfer processes, the performance of a TM bio-photoanode is significantly affected by the TM film quality. Thus, in this study, electrospraying was employed to deposit TMs with enhanced control of the thickness and uniformity of TM coating on metal electrodes. In particular, we investigated how both the quality of TM films and the magnitude of PE currents were influenced by electrospraying time, substrate motion, solution feed rates, TM concentration, and addition of graphene oxide (GO) nanosheets. Finally, to assess the feasibility of TM electrospraying as a scalable fabrication method, TMs were electrosprayed on $5 \times 5\,cm^2$ size films of indium tin oxide (ITO)-coated polyethylene naphthalate (PEN) (ITO-PEN). The coating uniformity was assessed by measuring PE currents from different locations of the TM-deposited ITO-PEN films.

1. Introduction

Photosynthesis of plant cells or photosynthetic algal cells converts solar energy into electrons with the quantum yield of nearly 100%. Thus, there have been many attempts to mimic or utilize the photosynthesis to harvest solar energy at high efficiency. In photosynthesis, water molecules are split and produce electrons, photosynthetic electrons (PEs). Then, the PEs are transferred electrochemically in a photosynthetic electron transfer chain through photosystem II (PS II), plastoquinone pools, cytochrome *b6f* complexes, and photosystem I (PS I) in the thylakoid membranes (TMs) inside the plant cells or algal cells. To extract PEs during the photosynthesis process, various approaches were investigated using living photosynthetic algal cells [1–3], isolated TMs [4–8], PSI [9,10], and PSII [11].

Compared to the approaches using PS II or PS I, use of TMs has several advantages such as process scalability, stability, and relatively easy isolation process [6]. Bio-photoanodes are in general fabricated by depositing isolated TMs on a metal electrode. The performance of a bio-photoanode is significantly influenced by the quality of the deposited TM films. The light absorption, charge transfer, and electrical conductivity determines the overall performance of PE collection by a TM bio-photoanode. So far, many efforts were made mainly to enhance the electrical properties of TM-based bio-photoanodes using nanomaterials such as carbon nanotubes [5] and osmium-based redox polymer [6]. In many cases, TMs were drop cast on a metal electrode non-uniformly. This often resulted in unreliable and unrepeatable performance of photosynthetic energy harvesting for large electrodes. Thus, to further develop the photosynthetic energy harvesting as practical applications, it is important to uniformly deposit the composite solutions of TMs and nanomaterials on a large-scale substrate.

In electrospraying, nanoscale droplets of a solution are ejected when electrostatic repulsion within the solution becomes larger than the surface tension of the solution. Electrospraying is identical with electrospinning in terms of the setup and operating principle. However, electrospraying requires a less viscous solution than a solution for electrospinning. Thus, ejected jet is easily destabilized to form nano droplets, and the highly charged droplets are self-dispersed in space [12]. Since the solution is ejected due to strong electrostatic repulsion

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