



Water oxidation-coupled, photoelectrochemical redox biocatalysis toward mimicking natural photosynthesis



Dong Heon Nam¹, Gyeong Min Ryu¹, Su Keun Kuk, Da Som Choi, Eun Jin Son, Chan Beum Park*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 335 Science Road, Daejeon 305-701, Republic of Korea

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ABSTRACT

Redox enzymes are industrially important for catalyzing highly complex reactions because of their excellent regio- and stereo-selectivity; however, broad application of redox enzymes has been often limited by the requirement of stoichiometric supply of cofactors such as β -nicotinamide adenine dinucleotide (NADH). Here, we report light-driven cofactor regeneration coupled with water oxidation by employing a photoelectrochemical cell platform consisted of a FeOOH/Fe₂O₃ photoanode and a black silicon photocathode. The FeOOH layer deposited on Fe₂O₃ surface decreased reaction barriers for water oxidation. The black silicon photocathode exhibited high photocurrent response and superior capacity to drive cofactor reduction. The cofactor regeneration yield in the photoelectrochemical cell was almost two-fold higher than that obtained in homogeneous system, which demonstrates that photoelectrochemical cell is a promising platform for redox biocatalytic reactions using water as an electron donor.

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1. Introduction

Catalytic reactions enable the synthesis of valuable chemicals from raw materials [1]. In many cases, however, conventional catalysts produce undesirable byproducts (e.g., stereoisomers), which requires additional separation or purification steps and increases production cost. On the contrary, biocatalytic reactions using enzymes exhibit high specificity, allowing selective synthesis of stereospecific isomers [2]. To date, however, broad application of oxidoreductases has been often limited by problems related to the supply of cofactors such as β -nicotinamide adenine dinucleotide (NADH) because of their high prices [3,4]. Since cofactors act as a reducing equivalent in redox biocatalytic reactions, efficient supply of cofactors is a key barrier for industrializing enzymatic processes for the synthesis of valuable fine chemicals. To solve this problem, many researchers have attempted to regenerate oxidized cofactors in situ [5–8]. As described in our previous report [9], photochemical method enables the regeneration of cofactors for biocatalytic reactions in a cost-effective and environmentally friendly manner by using abundant solar energy; however, the use of organic sacrificial

agents such as triethanolamine as an electron donor accumulates their oxidized forms in the reactor.

In green plants, water serves as an electron donor for photosynthesis that converts solar energy into chemical energy through a series of photo-induced electron transfer between photosystem II and I (Fig. 1). Inspired to natural photosynthesis, many efforts have been devoted to couple redox biocatalytic reactions with water oxidation in a homogeneous system; however, only a few studies were reported because of the difficulties (e.g., back electron transfer, charge recombination) in kinetic coupling between water oxidation and biocatalytic reactions [10,11]. In this regard, we expect that a photoelectrochemical (PEC) cell, which convert solar energy and water to valuable chemicals by mimicking natural photosynthesis, is a promising platform for integrating biocatalytic reactions with water oxidation reaction. Here, we first report on PEC cell-based photoelectrochemical NADH regeneration with water as an electron donor. As illustrated in Fig. 1, the PEC cell is configured with FeOOH-deposited hematite (FeOOH/Fe₂O₃) photoanode and black silicon (b-Si) photocathode. Hematite holds great promise as a photoanode material, satisfying the requirements of sufficient visible-light absorption, high stability, earth-abundant, nontoxic, and low cost [12]; however, water oxidation efficiency with hematite remains low due to poor electrical conductivity, short hole diffusion length, and the short lifetime of carriers [13,14]. So far, several attempts have been made to enhance the perfor-

* Corresponding author.

E-mail address: parkcb@kaist.ac.kr (C.B. Park).

¹ These authors contributed equally to this work.

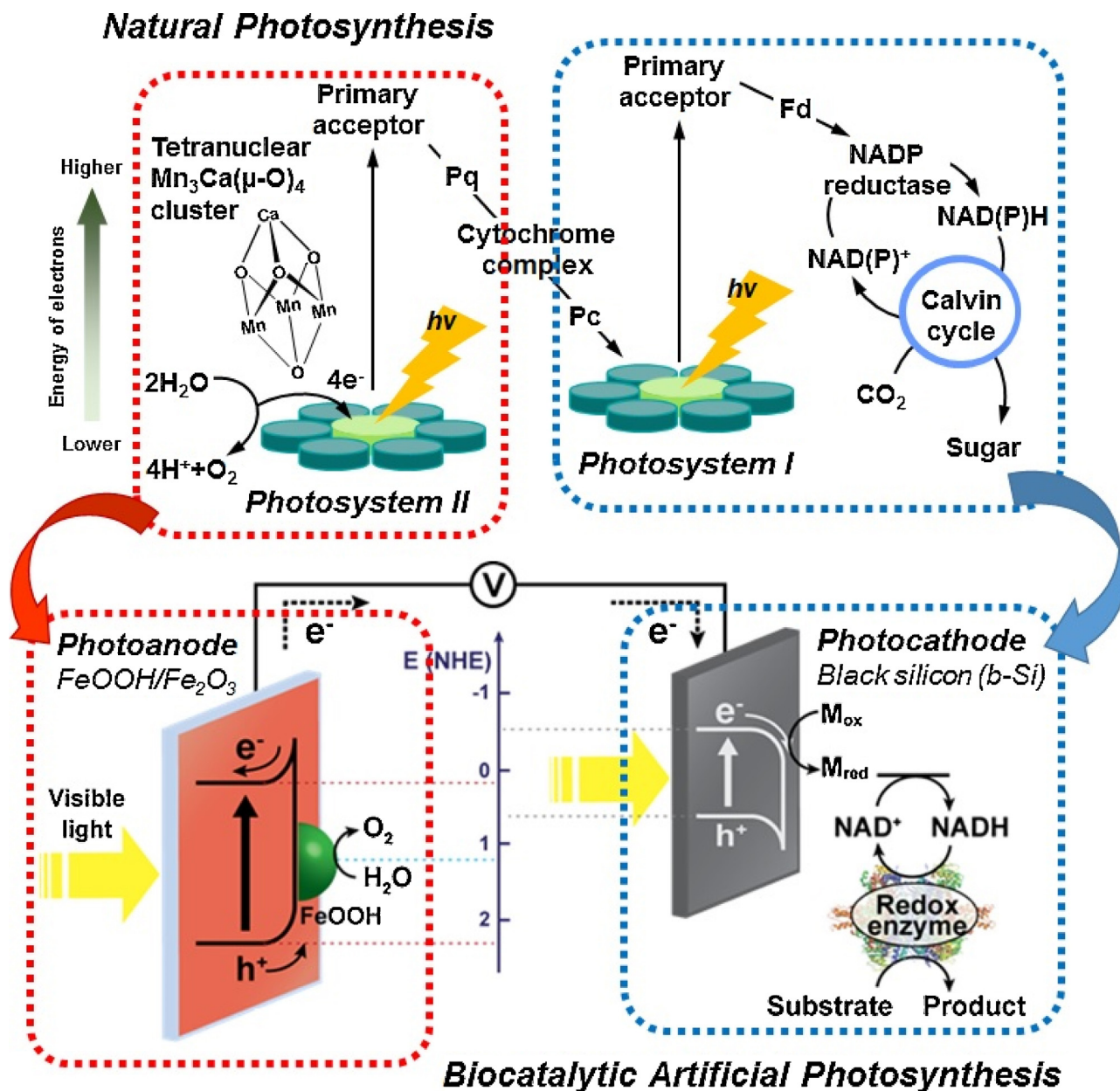


Fig. 1. Illustration of PEC cell-based photoelectrochemical NADH regeneration and redox biocatalysis using water as an electron donor, which mimics natural photosystems. Under visible light illumination, water is oxidized by photogenerated holes at the photoanode (FeOOH/Fe₂O₃) and serves as an electron donor. Photoexcited electrons are transferred to the photocathode (black silicon), followed by reduction of NAD⁺ to NADH via rhodium-based mediator ($\text{M} = [\text{Cp}^*\text{Rh}(\text{bpy})\text{H}_2\text{O}]^+$, Cp* = C₅Me₅, bpy = 2,2'-bipyridine). Ultimately, the excited electrons from reduced NAD⁺ are delivered to NADH-dependent redox enzymes, such as L-glutamate dehydrogenase (GDH), for biocatalytic synthesis.

mance of hematite by applying oxygen evolution catalysts (OECs) to the hematite surface [15], performing hematite-doping with other elements [16], and controlling morphology [17]. In this study, we deposited iron oxyhydroxide (FeOOH) on hematite surface, which facilitates water oxidation kinetics by taking up holes and suppressing electron-hole recombination on hematite [18]. For NADH regeneration and redox biocatalytic synthesis, we utilized b-Si photocathode having large surface area and near-unity absorbance [19]. L-Glutamate dehydrogenase (GDH) was used as a model oxidoreductase for redox enzymatic reaction coupled with PEC cell-based NADH regeneration. Using the PEC cell platform, we achieved high rates of NAD⁺ reduction and GDH-catalyzed L-glutamate synthesis with water as an electron donor.

2. Experimental

2.1. Materials

Iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, sodium nitrate, cobalt nitrate, iron(II) sulfate heptahydrate, β -nicotinamide adenine dinucleotide hydrate (NAD⁺), ammonium sulfate, α -ketoglutaric acid, L-glutamic dehydrogenase, and fluorine-doped tin oxide (FTO) glass (surface resistivity $\sim 7 \Omega/\text{sq}$) were purchased from Sigma-Aldrich (USA). Lightly doped (1–10 $\Omega \text{ cm}$) p-type silicon wafers (100) were obtained from Tasco (Korea). The rhodium-based mediator ($\text{M} = [\text{Cp}^*\text{Rh}(\text{bpy})\text{H}_2\text{O}]^+$, Cp* = C₅Me₅, bpy = 2,2'-bipyridine) was synthesized according to the literature [20].

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