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# Near-complete charge separation in tailored $BiVO_4$-based heterostructure photoanodes toward artificial leaf

Jin Wook Yang [a], Ik Jae Park [c], Sol A. Lee [a], Mi Gyoung Lee [a], Tae Hyung Lee [a], Hoonkee Park [a], Changyeon Kim [a], Jaemin Park [b], Jooho Moon [b], Jin Young Kim [a,*], Ho Won Jang [a,d,*]

[a] Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul, 08826, Republic of Korea
[b] Department of Materials Science and Engineering, Yonsei University, Seoul, 03722, Republic of Korea
[c] Department of Applied Physics, Sookmyung Women's University, Seoul 04310, Republic of Korea
[d] Advanced Institute of Convergence Technology, Seoul National University, Suwon 16229, Republic of Korea

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ABSTRACT

As an artificial leaf, a tandem device for zero-bias solar water splitting is a capable solution for practical hydrogen production. Despite a promise, poor charge transport of $BiVO_4$ hampers photoelectrochemical performances under front-side illumination, which is a hindrance to the tandem system. Herein, we design a new photoanode comprising nanoporous $BiVO_4$ and $SnO_2$ nanorods focused on the charge separation via structural and interfacial engineering. $BiVO_4/SnO_2$ photoanode exhibits not only remarkable charge separation efficiency of 97% but also, by loading NiFe as a co-catalyst for water oxidation, high photocurrent density of 5.61 mA $cm^{-2}$ at 1.23 V versus the reversible hydrogen electrode under front-side 1 sun illumination. Consequently, a tandem cell comprising $NiFe/BiVO_4/SnO_2$ photoanode and perovskite/Si tandem solar cell generates an operating photocurrent density of 5.90 mA $cm^{-2}$ with a solar-to-hydrogen conversion efficiency of 7.3% in zero-bias. This work would be a significant step to develop spontaneous solar hydrogen production.

## 1. Introduction

Photoelectrochemical (PEC) water splitting, which directly converts sunlight into hydrogen fuel, is one of the most sustainable solutions to stockpile solar energy. However, low solar-to-hydrogen (STH) conversion efficiency compared to its potential, has been a barrier to the commercialization, unlike a highly efficient photovoltaic (PV) system. The photovoltage generated by a single photoanode is insufficient to reach a required voltage (1.23 V + overpotential) for the water splitting reaction, resulting in a nonspontaneous reaction requiring external bias [1,2]. In this single absorber system, a trade-off between photovoltage generation and light absorption according to the bandgap limits improving PEC performances [3,4]. Thus, a tandem system consisting of dual absorbers with an optimal bandgap combination has been widely studied to maximize light harvesting by separating each absorption wavelength range [5–10]. A PEC-PV tandem system, especially, is favorable for spontaneous PEC water splitting in zero-bias due to the high STH conversion efficiency in terms of photovoltage production [2]. In this system, high photocurrent density in water oxidation of front photoanode is key to maximize the efficiency of the entire cell.

$BiVO_4$, which is one of the most promising photoanode materials, has a suitable band gap and band edge position for water oxidation, delivering a high theoretical photocurrent density of 7.5 mA $cm^{-2}$ and STH conversion efficiency of 9.2% [11–13]. These PEC characteristics, however, markedly diminish under front-side illumination, and this issue hinders the implementation of PEC-PV tandem cell that requires high front PEC performance. Such a drawback is caused by the slow electron transport limiting the photocurrent generation of $BiVO_4$ [14,15]. Namely, the short carrier diffusion length (~70 nm) of $BiVO_4$ inhibits charge separation [16]. To enhance the charge separation efficiency of $BiVO_4$, two representative strategies are used; the first one is the nanostructuring of $BiVO_4$ [11,17,18]. Kim et al. fabricated a nanoporous $BiVO_4$ photoanode with charge separation efficiency of 90% [19], and Kuang et al. found an optimal average diameter (≈120 nm) of $BiVO_4$ to maximize PEC properties under front-side illumination [15]. The distance between the electrode inside and the electrolyte interface was structurally engineered as much the carrier diffusion length to make efficient charge transport without a reduction of light absorption. The

* Corresponding authors.
*E-mail addresses:* jykim.mse@snu.ac.kr (J.Y. Kim), hwjang@snu.ac.kr (H.W. Jang).

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