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Communication

Design of a Monolithic Photoelectrochemical Tandem Cell for Solar Water Splitting with a Dye-sensitized Solar Cell and $WO_3/BiVO_4$ Photoanode

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ABSTRACT: Photoelectrochemical cell (PEC) is one of the attractive ways to produce clean and renewable energy. However, solar to hydrogen production via PEC system generally requires high external bias, because of material's innate electronic band potential relative to hydrogen reduction potential and/or charge separation issue. For spontaneous photo-water splitting, here, we design dye-sensitized solar cell (DSSC) and their monolithic tandem cell incorporated with a $BiVO_4$ photoanode. $BiVO_4$ has high conduction band edge potential and suitable band gap (2.4eV) to absorb visible light. To achieve efficient $BiVO_4$ photoanode system, electron and hole mobility should be improved, and we demonstrate a tandem cell in which $BiVO_4/WO_3$ film is connected to cobalt complex based DSSC.

Solar to hydrogen generation has been suggested via photoelectrochemical (PEC) water splitting cell. For spontaneous water splitting, the photoelectrode material should satisfy electronic band positions which include water redox reaction potentials and its band gap wants to be ~ 2.0 eV for efficient sunlight absorption. Up to now, $BiVO_4$ is one of the most actively studied photoanode materials for solar water splitting, but short electron diffusion length[1], and slow electrokinetics[2] of oxygen evolution reaction should be improved. Doping[3], morphological control[4], heterojunction with other semiconductors[5], or cocatalyst loading was introduced to solve the issues[6] in $BiVO_4$. We have demonstrated highly active $BiVO_4/WO_3$ heterojunction photoanode in the previous work[7]. However, unfortunately, the band positions of $BiVO_4/WO_3$ heterojunction are still not ideal to split water, and it requires external bias potentials[8]. To supply the incomplete bias potential, the photoanode can be coupled with a photovoltaic (PV) cell. Considering the efficient absorption of the incident light, the series tandem connection between photoelectrode and PV cell is favorable to the parallel connection.

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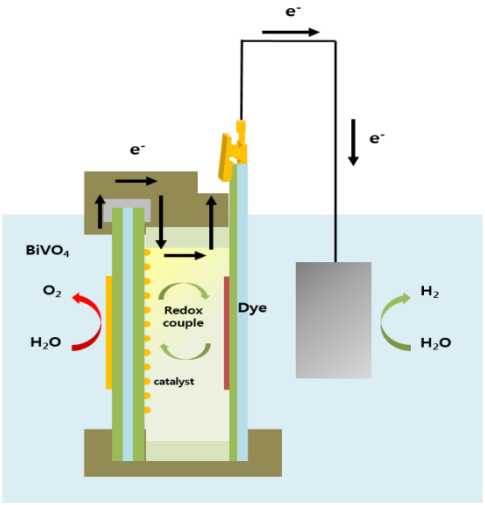

Scheme 1. Structures of PEC-PV tandem cell with $BiVO_4/WO_3$ photoelectrode and dye-sensitized solar cell

Scheme 1 shows a PEC-PV tandem cell in which a dye-sensitized solar cell (DSSC) can utilize the transmitted light after through $BiVO_4/WO_3$ photoanode. We firstly, characterize optical properties of $BiVO_4/WO_3$ photoanode and DSSC, respectively, to balance the light absorption. Especially, four different types of dye molecules (D35, Y123, MK2, and YD2-o-C8) have been used for DSSC.

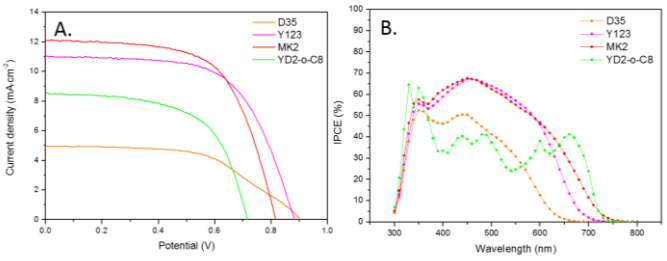

Figure 1. I-V curves of four different types of DSSCs depending on the dye molecules (A) and their IPCE measurements (B).

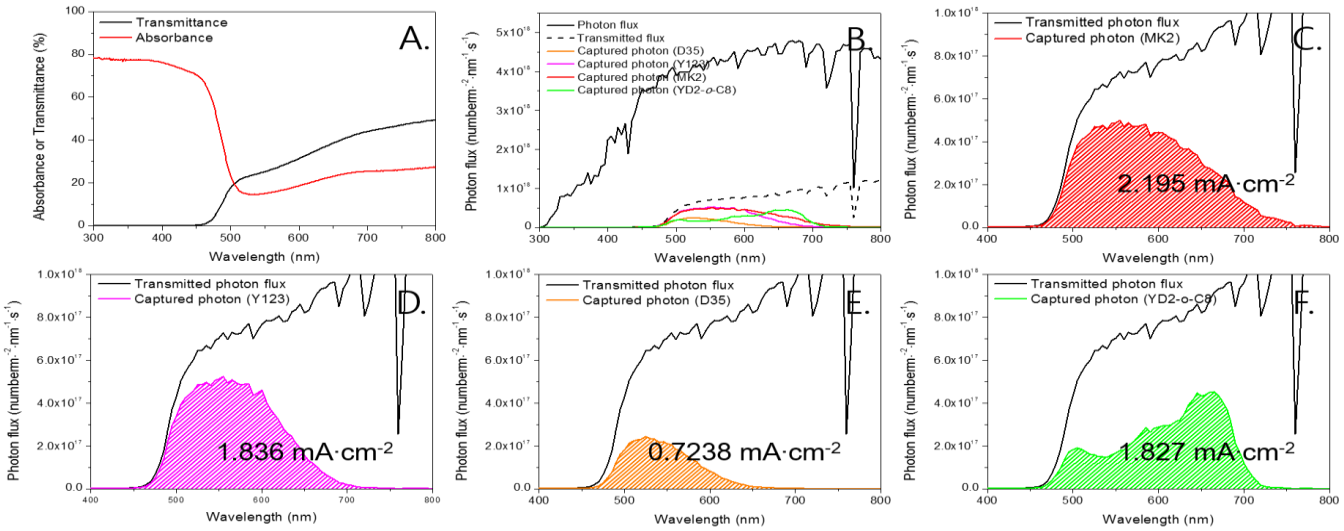

Figure 2. Absorbance and transmittance of $BiVO_4/WO_3$ photoanode (A). Photon flux of 1 sunlight and captured photons by DSSCs (B). The J_{sc} was calculated from the captured photon in (C), (D), (E), and (F) for MK2, Y123, D35, and YD2-o-C8, respectively.

Figure 1 shows I-V curves of DSSCs under the simulated sunlight (AM 1.5) and their incident photon-to current efficiency (IPCE) measurements depending on the types of the dye molecules. The open circuit voltage (V_{oc}) and short circuit current (J_{sc}) varied (Figure 1A) because dye molecules influence on the light absorption range and the Fermi level of the dye-sensitized TiO_2 photoanode. MK2 showed the highest J_{sc} due to high quantum efficiency (Figure 1B) in the longer wavelength region (> 650 nm). Meanwhile, Y123 or D35 were advantageous to have high V_{oc} values.

To understand PEC-PV tandem cell performance, we estimate J_{sc} of DSSCs when combined with $BiVO_4/WO_3$ photoanode. Absorbance and transmittance of $BiVO_4/WO_3$ photoanode were measured (Figure 2A) because the incident light passed through the photoanode first before reaching the DSSC. The J_{sc} of the DSSC in the combined tandem cell was calculated from IPCE of DSSC ($IPCE_{DSSC}$) and transmittance of the $BiVO_4/WO_3$ ($\%T_{BiVO_4/WO_3}$) depending on the incident wavelength (Equation 1)[9].

$$\int \text{Charge of electron} \times \text{Photon flux of sunlight}(\lambda) \times \%T_{BiVO_4/WO_3}(\lambda) \times IPCE_{DSSC}(\lambda)\, d\lambda$$

The captured photon by the DSSC is plotted in Figure 2B, and each detail integrated J_{sc} values of the DSSC were estimated in Figure 2C-F. Because the $BiVO_4/WO_3$photoanode absorbed most of visible light region shorter than 500 nm, the DSSC can utilize only the rest of visible light and near-IR light. YD2-o-C8 dye ($J_{sc,YD2\text{-}o\text{-}C8}$ = 1.827 $mA{\cdot}cm^{-2}$) showed similar integrated J_{sc} of DSSC in the tandem cell compared to Y123 dye ($J_{sc,Y123}$ = 1.836 $mA{\cdot}cm^{-2}$) although J_{sc} values of separate DSSC showed large difference (Figure 1A). This is because YD2-o-C8 dye captured near IR light region more efficiently than Y123 dye. Due to the light absorption capability in ~ 650 nm, MK2 still showed the highest $J_{sc,\ MK2}$= 2.195 $mA{\cdot}cm^{-2}$ even under the tandem cell.

V_{oc} is another important parameter in the tandem cell for solar water splitting because it determines the bias potential that can supply to the PEC cell. Both of J_{sc} and V_{oc} values have to show large value for the tandem PEC cell application. Hence, Y123 dye sensitized solar cell is selected to be coupled with the $BiVO_4/WO_3$ photoanode, later in this study.

Figure 3 showed the I-V performance of Y123 dye-sensitized solar cell which was masked with the Co-Pi/$BiVO_4/WO_3$ photoanode. The surface of the photoanode was decorated with Co-Pi cocatalyst to improve the water oxidation activity under the same biased potential which will finally improve the spontaneous water splitting. Figure 3 showed the measured J_{sc} value (1.78 $mA{\cdot}cm^{-2}$) of DSSC in the tandem cell was close to the estimated ($J_{sc,Y123}$ = 1.836 $mA{\cdot}cm^{-2}$) one according to Equation 1. The difference can be originated from the decoration of Co-Pi which can block the incident light as well. V_{oc} of the DSSC was diminished slightly from that of the 1 Sun condition, due to weakened incident light intensity to the DSSC. The operating current (J_{op} =1.44 $mA{\cdot}cm^{-2}$) of the tandem PEC cell can be estimated from the intersection between the I-V curve of the DSSC and that of the photoanode because the current flow should be balanced.

Finally, the DSSC/photoanode tandem cell was tested for solar water splitting with a two-electrode configuration, using Pt as a counter electrode (Figure 4). Figure 4A shows the onset potential of Co-Pi/$BiVO_4/WO_3$ photoanode at ~ 0.4V, implying water splitting with this photoanode requires at least 0.4 V of biased potential even under sunlight irradiation.

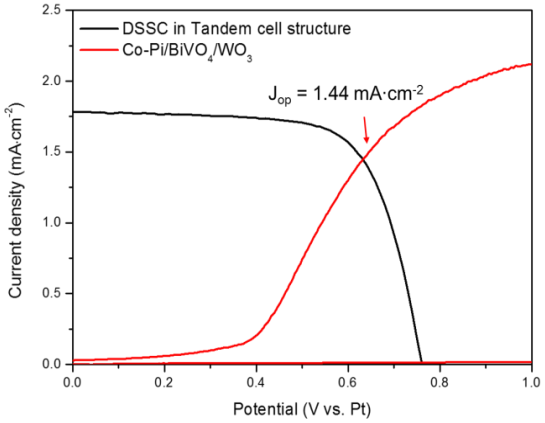

Figure 3. I-V curve of Co-Pi/$BiVO_4/WO_3$ photoanode and that of Y123 dye-sensitized solar cell in the tandem PEC cell configuration. The respective I-V curve was measured with the tandem PEC cell.

However, I-V curve of the Co-Pi/$BiVO_4/WO_3$-DSSC tandem cell was shifted toward negative potential and had the onset potential of the photocurrent ~-0.4 V. This largely negative shift was obtained by the photovoltage generated from the Y123 DSSC, which makes the tandem cell possible to spontaneous water splitting under only solar light irradiation. However, the short-circuit photocurrent (1.094 mA·cm^{-2} at 0 V) of tandem cell is not exactly matched predicted one, J_{op} (1.44 mA·cm^{-2}), probably due to a series resistance between PEC and DSSC connector.

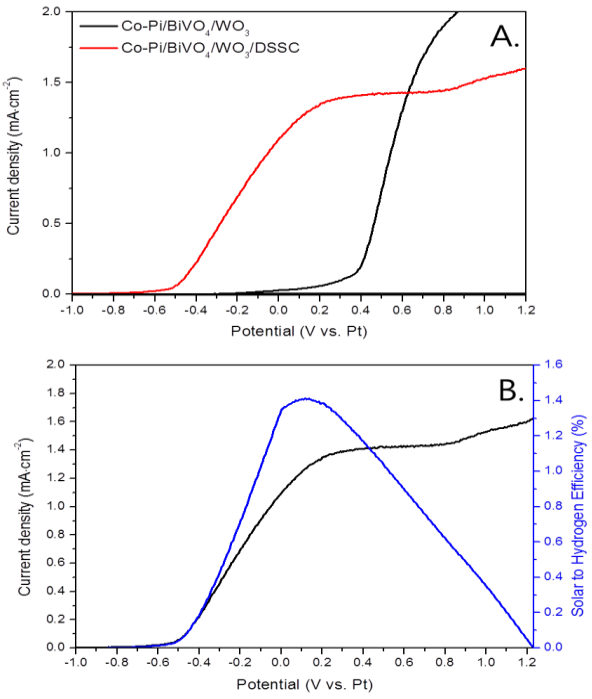

Figure 4. (A) The I-V curve of $BiVO_4/WO_3$ photoanode and (B) $BiVO_4/WO_3$ photoanode/Y123 dye sensitized solar cell.

Finally, we calculate the applied bias photon to current efficiency (ABPE) of from equation 2[10] (Figure 4B). The maximum ABPE was 1.4% at 0.1 V, and 1.34% at 0 V.

$$\text{ABPE}\ (\%) = \frac{(\text{photocurrent} \times 1.23 - \text{applied bias})}{\text{light intensity}} \times 100 \qquad (2)$$

In conclusion, we design DSSC with four different types of dyes, D35, Y123, MK2, and YD2-o-C8 for a PEC-PV tandem cell, especially with $BiVO_4/WO_3$ photoanode. Unlike 1 sun irradiation condition, the tendency J_{sc} values with the DSSCs in the tandem cells were estimated differently because the incident light was passed through the $BiVO_4/WO_3$ photoanode beforehand. From the IPCE of the DSSC and transmittance of the $BiVO_4/WO_3$ photoanode, Y123 dye-sensitized solar cell was considered the most favorable. The monolithically incorporated tandem cell with Co-Pi/$BiVO_4/WO_3$ photoanode and Y123 DSSC showed about 800 mV of cathodic shift of I-V curve as compared to the Co-Pi/$BiVO_4/WO_3$ photoanode cell. This PEC-PV tandem cell can split water spontaneously under solar light irradiation successfully, with 1.4 % of ABPE at 0.1 V. The way to find suitable dye for the tandem structured DSSC is considered useful to design for PEC-PV tandem cell or other optical tandem device.

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KEYWORDS: $BiVO_4$, dye-sensitized solar cell, tandem cell, monolithic cell, water splitting

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SUPPORTING INFORMATION

Experimental procedures and characterization. This material is available free of charge via the Internet at http://XXXXXX

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