Water Splitting Photovoltaic-Photoelectrochemical GaAs/InGaAsP - WO3/BiVO4 Tandem Cell with Extremely Thin Absorber Photoanode Structure


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We demonstrate highly efficient solar hydrogen generation via water splitting by photovoltaic-photoelectrochemical (PV-PEC) tandem device based on GaAs/InGaAsP (PV cell) and WO3/BiVO4 core/shell nanorods (PEC cell). We utilized extremely thin absorber (ETA) concept to design the WO3/BiVO4 core/shell heterojunction nanorods and obtained the highest efficiencies of photo-induced charge carriers generation, separation and transfer that are possible for the WO3/BiVO4 material combination. The PV-PEC tandem shows stable water splitting photocurrent of 6.56 mA cm⁻² under standard AM1.5G solar light that corresponds to the record solar-to-hydrogen (STH) conversion efficiency of 8.1%.

Keywords: Photocatalysis, Photovoltaics, Renewable energy, Nanorods, WO3, BiVO4, Heterojunction.

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1. INTRODUCTION

Solar photovoltaics (PV) industry is growing rapidly and is going to achieve 235 gigawatts (GW) level of cumulative capacity installed worldwide by the end of 2015. This growth is stimulated by feed-in tariffs initiatives that were implemented by a number of governments in order to provide economic feasibility for investments into renewable energy. However, the distributed generation of electricity by residential PV systems and commercial PV power plants is already causing instabilities of electric grid due to variability of the PV output. For that reason the storage of solar energy in a form of hydrogen that is generated via PV assisted photocatalytic water splitting is considered as a promising approach to compensate intermittency of the PV electricity supply with additional benefit of obtaining zero greenhouse gas emission fuel for transportation vehicles and aircrafts.

Fig. 1 – Schematic illustration of the PV-PEC tandem device where the PV cell operates under reflected light from the PEC cell. (a) Utilization of the incident AM1.5G solar light by the tandem device that is calculated from external quantum efficiency (EQE) spectra of the PV-PEC tandem sub-cells. (b) Cross section SEM image of the PEC cell based on core/shell WO3/BiVO4 nanorods.

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Since the discovery of photoelectrochemical water splitting on TiO$_2$ by Fujishima and Honda [1], the photocatalytic decomposition of water by solar light has been considered as the most promising green technology for the generation of hydrogen. However, the solar-to-hydrogen conversion efficiency (STH) of TiO$_2$ is fundamentally limited to 1.3% due to its wide band gap of 3.2 eV that allows utilization of the ultraviolet light only. Thus the development of photocatalytic materials with narrower bandgap that is sensitive to the visible part of the solar spectrum is highly desirable.

Bismuth vanadate (BiVO$_4$) is one the most promising photocatalytic materials with direct bandgap of 2.4 eV and theoretical STH conversion efficiency of 9.2%. Unfortunately BiVO$_4$ is characterized by a short carrier diffusion length ($L_d$) of around 70 nm. As a result, the efficient generation of photocarriers is compensated by their fast recombination, which is the main reason for the unsatisfactory photocatalytic efficiency of BiVO$_4$. One possibility to compensate for the short $L_d$ is to use an extremely thin absorber (ETA) heterojunction structure, where the BiVO$_4$ absorber layer is thinner than the $L_d$ while its optical thickness is reestablished by a structured configuration with a high aspect ratio (as illustrated in the Fig. 1).

In our previous work we have already demonstrated PEC cell with the ETA structure based on WO$_3$/BiVO$_4$ core/shell nanorods with record water splitting efficiency approaching 8% in a self-biased water splitting PEC-PV tandem device [2]. In this work we report detailed characterization of the PV-PEC device and discuss mechanism of the water splitting process.

2. EXPERIMENTAL

We fabricated the PEC photoanode by a combination of glancing angle deposition (GLAD) of WO$_3$-NRs and electrochemical deposition (ED) of BiVO$_4$ and cobalt phosphate co-catalyst. For the details about fabrication of WO$_3$-NRs by GLAD see our previous works [2, 3]. At first, we sputtered a three layer stack film of ITO (150 nm) / Pt (50 nm) / ITO (150 nm) on a fused silica substrate. The stack film had low sheet resistivity of 4 Ω/□ due to the encapsulated Pt layer. The Pt layer simultaneously functioned as a mirror reflector of the incident light. Then we changed the sample stage position to the GLAD regime with the deposition flux angle of 85º to the substrate normal and constant substrate rotation of 45 rpm. The WO$_3$-NRs with the length of 2.5 µm were deposited by reactive sputtering at 0.3 Pa of O$_2$: Ar (9.6 : 11 sccm) working gas mixture and then crystallized by annealing in air at 575 °C during 4.5 h. The BiVO$_4$ layer with the thickness of 30 nm was electrodeposited over WO$_3$-NRs by the method of Seabold et al. [4] from 10 mM Bi(NO$_3$)$_3$ in 35 mM VOSO$_4$ electrolyte adjusted to pH = 4.7 at 0.21 V vs Pt counter electrode. Then the photoanodes were annealed in air at 500 °C for 2 hours to obtain crystalline monocline BiVO$_4$. The cobalt phosphate (CoP) co-catalyst was deposited on the BiVO$_4$ surface by photo-assisted electrodeposition method according to the recipe of Li et al.[5].

The PV cell consisted of two mechanically stacked GaAs (E$_g$ = 1.42 eV) and InGaAsP (E$_g$ = 1.0 eV) solar cells prepared by solid-state MBE followed by epitaxial lift-off (ELO) and then interconnected through aligned Pd nanoparticle arrays (Fig. 1) according to the previous works of Makita et al. [6, 7], Sugaya et al. [8, 9] and Mizuno et al. [10]. The PV cell was encapsulated by a glass cap and assembled on V-shape support with the PEC cell located at 45º. The performance of the PV-PEC tandem device was evaluated by following standard protocol for water splitting cells [11].

3. RESULTS AND DISCUSSION

Fig. 1 illustrates the concept of the PV-PEC tandem device and shows utilization of solar light calculated from external quantum efficiencies (EQE) of the PEC-PV tandem sub-cells. The cross-section and top-view SEM images in Fig. 1b and Fig. 2a,b reveal that GLAD formed well-separated WO$_3$-NRs with diameters of 150 ~ 200 nm. The subsequent ED of the BiVO$_4$ layer proceeded in a “layer-plus-island” Stranski-Krastanov growth mode with formation of hemispherical clusters. The characteristic peaks in the XRD spectrum (Fig. 2c) confirm monoclinic phases of WO$_3$ and BiVO$_4$.

![Fig. 2 – (a) and (b) show SEM images of WO$_3$-NRs and WO$_3$-NRs/BiVO$_4$, respectively, while (c) shows XRD spectrum of the ITO/Pt/ITO/WO$_3$-NRs/BiVO$_4$ photoanode.](image-url)
Fig. 3 shows schematic energy diagram of the WO₃-NRs/BiVO₄+CoPi photoanode and mechanism of the PV-assisted photocatalytic water splitting process. The solar light with the energy over 2.4 eV is mainly absorbed in the BiVO₄ layer. Although BiVO₄ layer is extremely thin, of around 30 nm, it is nevertheless very efficient absorber due to the direct bandgap of BiVO₄ and enhanced light trapping in the high aspect ratio nanostructures. From a ray-optics perspective, the light trapping enhancement at rough interfaces is given by 4n², where n is refractive index of the absorber layer [12]. Since the refractive index of BiVO₄ is close to 2.5 [13] we can expect significant light trapping in the BiVO₄ nanostructured layer. In contrast, the WO₃-NRs give small contribution to the overall light absorption due to indirect bandgap of WO₃. Thus the WO₃-NRs mainly function as highly conductive cores for the electron transport.

![Energy Diagram](image)

Fig. 3 – Schematic energy diagram and mechanism of the PV-assisted photocatalytic water splitting by the WO₃-NRs/BiVO₄+CoPi photoanode.

The electron-hole pairs generated in the BiVO₄ layer are separated at the WO₃/BiVO₄ heterojunction interface that has type II band alignment. The electrons are effectively transferred to the ITO/Pt/ITO underlayer via highly conductive WO₃-NRs cores. The holes remained in the BiVO₄ layer are transferred to co-catalyst CoPi clusters on the BiVO₄ surface and participate in the oxygen evolution half-reaction (OER). The ETA structure of the core/shell WO₃-NRs/BiVO₄ photoanode can be tuned to achieve near theoretical water splitting photocurrent by separate optimization of WO₃-NRs length and thickness of the BiVO₄ absorber layer. In our case the optimized thickness of the BiVO₄ layer was 30 nm that is more than two times thinner than the Lₜ. Simultaneously, the 2.5 μm long core/shell WO₃/BiVO₄ nanorods trap all the incoming light in the BiVO₄ layer with the energy above its bandgap.

Spontaneous water splitting requires sufficient offsets of conduction and valence bands of the photocatalyst to provide suitable overpotentials for H₂ and O₂ evolution half-reactions. Unfortunately, the position of the BiVO₄ conduction band does not fulfill that condition, and the photoanode needs an additional bias potential provided by a PV cell to drive the H₂ evolution half-reaction. Previously, mechanically stacked tandems, based on a dye-sensitized solar cell (DSSC) with Fe₃O₃ or WO₃ photoanodes [14], and monolithic tandems, based on single- or double-junction a-Si solar cells with BiVO₄:Mo+CoPi photoanode layers [15], demonstrated self-biased photocurrents of 1.34, 2.23, 3.0 and 4.0 mA cm⁻², respectively. In our case we used a double-junction GaAs/InGaAsP PV cell that operated under the light reflected from the photoanode. In this configuration, the portion of the solar light with the energy below 2.4 eV is transmitted to the Pt underlayer and then reflected toward the PV cell located at 45° with respect to the PEC photoanode.

The photoelectrochemical characterizations of the WO₃-NRs/BiVO₄+CoPi photoanode were conducted according to the standard characterization protocol for PEC cells [11] in potassium phosphate buffer solution (pH = 7) by a two electrode method with the bias applied vs Pt counter electrode. The simulated AM1.5G solar light was adjusted by using an NREL calibrated photodetector.

![Photocurrent vs Voltage](image)

Fig. 4 – (a) I-V characteristics of the PV cell (red) and the PEC cell (green) measured in the tandem configuration where the PV cell operated under the light reflected from the PEC cell. (b) I-V characteristics of the PV cell: (red) in the tandem configuration under the light reflected from the PEC cell, (blue) without the PEC cell in the tandem assembly, (black) at dark conditions and (pink) under normal incident light. The photocurrent is displayed in absolute values by using Log scale. All characterizations were performed by using standard AM1.5G light provided by a solar simulator with the light intensity calibrated to 1 sun.

The I-V characteristics of the PV and the PEC cells intersect around 1 V at 6.56 mA (Fig. 4a), which approaches 90% of the theoretically possible photocurrent value for BiVO₄. The STH efficiency of 8.1% is obtained by multiplying the photocurrent and the water splitting energy of 1.23 eV. To the best of our
knowledge, this is the highest up to date efficiency reported for water splitting PV-PEC tandems. The PV and PEC cells with dimensions of 4 mm × 4 mm and 4 mm × 5.65 mm (i.e. √2 × 4 mm), respectively, were assembled on a V-shape support in such a way that the PEC cell was located at 45° to the incident light while the PV cell was located parallel to the incident light. As a result the illuminated area of the tandem device was equal to 4 × 4 mm² and the PV cell operated only under the light reflected from the photoanode.

We also measured I-V characteristics of the PV cell without the PEC cell in the tandem assembly to confirm that the PV cell is oriented parallel to the incident light and does not receive additional light from parasitic reflections (Fig. 4b). Indeed, the I-V characteristics of the PV cell in the absence of the PEC cell in the tandem assembly were very close to the ones measured at dark conditions.

![Figure 5](image)

**Fig. 5** – (a) Faradaic efficiencies $\xi$ and (b) specific quantities of evolved H₂ (red) and O₂ (black) gases per illuminated device area measured by gas chromatography with (c) simultaneously recorded photocurrent density $J_p$. The dashed lines correspond to the theoretical quantities of H₂ (e/2) and O₂ (e/4) gases that were calculated from the total charge by integrating the measured photocurrent $J_p$. The faradaic efficiencies $\xi$ are calculated as ratios between the actually measured and the theoretically calculates quantities of the evolved gases.

In order to confirm that the measured photocurrent is utilized for the water splitting process, we directly measured the quantities of H₂ and O₂ evolved in an airtight reactor by gas chromatography. Fig. 5b shows specific quantities of evolved O₂ and H₂ gases while Fig. 5c shows simultaneously recorded photocurrent density. The H₂ and O₂ evolved at stoichiometric ratio with the H₂ generation rate approaching 102 µmol h⁻¹ cm⁻². The $J_p$-time profile was used to calculate the theoretical quantities of the evolved gases based on the total charge passed. Faradaic efficiencies ($\xi$) were calculated as ratios between the actually measured and the theoretically calculated quantities of the evolved gases. The faradaic efficiencies reach 80% within the first 15 minutes and later saturate at ~85%, which is a typical value for reactors with a single compartment, where the oxygen evolved from the photoanode can undergo a partial back reaction at the Pt counter electrode.

Fig. 1a reveals that the reflectance of the photoanode was only around 60% in the wavelength region >516 nm mainly due to the light scattering in the nanostructured photoanode. Nevertheless, the highly efficient GaAs/InGaAsP PV cell was able to generate the matching photocurrent even under the weak reflected light. Such high optical losses can be avoided in future by using a dichroic mirror that can split and guide dedicated portions of the solar spectrum separately to the PV cell and to the PEC cell.

The main advantage of the PV-PEC tandem configuration in comparison to the simple combination of PV cell and water electrolysis is the relaxed requirement for open-circuit potential of the PV cell. Direct electrolysis of water requires rather high overall potential of 1.6-2.0 V due to the high overpotential of oxygen evolution half-reaction that has to be compensated in addition the theoretical water splitting potential of 1.23 V. In contrast, our WO₂-NRs/BiVO₄+CoPi PEC cell requires a much lower bias of around 1 V that is in the range of recently developed inexpensive perovskite solar cells with open-circuit potential of 1.15 V [16]. The combination of a dichroic mirror and an inexpensive PV cell with ordinary performance characteristics can substitute expensive GaAs/GaAlAsP PV cell in the water splitting PV-PEC tandem device. Therefore, we believe that an economically viable PV-PEC tandem device based on a WO₂-NRs/BiVO₄+CoPi photoanode with STH of around 8% can be realized in the near future.

4. CONCLUSIONS

In conclusion, we utilized an extremely thin absorber (ETA) concept to fabricate a highly efficient water splitting photoelectrochemical (PEC) cell based on core/shell WO₂-NRs/BiVO₄+CoPi and combined it in tandem device with double heterojunction GaAs/InGaAsP photovoltaic (PV) cell. The PV-PEC tandem device demonstrated ultimate water splitting photocurrent of 6.56 mA under simulated AM1.5G solar light that is close to 90% of the theoretically possible photocurrent for BiVO₄ and corresponds to the solar-to-hydrogen (STH) conversion efficiency of 8.1%. To the best of our knowledge, this is the highest water splitting efficiency reported up to the date among all PV-PEC tandem devices.

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