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RAPID COMMUNICATION

Unassisted photoelectrochemical water splitting beyond 5.7% solar-to-hydrogen conversion efficiency by a wireless monolithic photoanode/dye-sensitised solar cell tandem device

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Abstract
Achieving the spontaneous evolution of hydrogen from photoelectrochemical (PEC) cells in water using solar light is a desirable but difficult goal. Here, we report a highly efficient wireless monolithic tandem device composed of bipolar highly transparent $BiVO_4$-sensitised mesoporous WO_3 films/Pt and a porphyrin-dye-based photoelectrode achieving 5.7% without any external bias. A sandwich infiltration process was used to produce a thin $BiVO_4$ layer coated onto mesoporous WO_3 films while preserving high transparency, enabling high photonic flux into the second dye-sensitised photoanode. In addition, the porphyrin-dye-sensitised photoanode with a cobalt electrolyte generated sufficient bias, realising highly efficient unassisted solar

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water splitting in the tandem cells. By combining the highly transparent $BiVO_4$-sensitised mesoporous WO_3 films with the state-of-the-art water oxidation catalyst and a single dye-sensitised solar cell with a high open circuit potential in a monolithic tandem configuration, an extraordinarily high solar-to-hydrogen (STH) conversion efficiency with spontaneous hydrogen evolution was obtained.

Introduction

In the four decades since the first report of photoinduced water splitting using a titanium dioxide (TiO_2) electrode, photoelectrochemical (PEC) water splitting has been achieved using various semiconductors [1]. However, a main requirement for cells that can induce spontaneous H_2 and O_2 evolution simultaneously with a single semiconductor photoelectrode is the discovery of a material with an appropriate bandgap of approximately 2.5 eV, a conduction band that is sufficiently negative for H_2 evolution and a valence band that is sufficiently positive for O_2 evolution. Unfortunately, devices capable of spontaneous gas evolution do not have high efficiency because the photoelectrodes (semiconductors) with a bandgap of 2.4–2.5 eV are only active under a limited solar spectra and require additional bias for overcoming over potentials [2,3].

One of the best approaches for solving this problem of single or heterojunction semiconductor PEC cells is the use of a tandem configuration. To date, various tandem device configurations have been reported. (1) A multi-junction silicon solar cell has been combined with hydrogen and oxygen evolution catalysts [4–6]. The best solar-to-hydrogen (STH) efficiency by this kind of configuration, up to 4.7%, was reported by Nocera and coworkers; however, fabrication of a multi-junction solar cell is too expensive for commercialisation. (2) A metal oxide semiconductor has been combined with a single or double junction silicon solar cell. Using tungsten-doped bismuth vanadate photoanode combined with a double-junction a-Si solar cell, 4.9% and 5.2% STH were achieved [7,8]. This method may have lower production costs than system (1) but remains too expensive for commercialisation. (3) The Si solar cell has been replaced with low-cost third generation solar cells such as dye-sensitised solar cells (DSSCs). The Sivular group recently achieved 3.1% STH by combining a WO_3 photoanode and DSSCs; however, external wiring makes this system complex, and the efficiency is still much lower than the 10% STH target [9]. Our research group recently reported a wireless WO_3/DSSCs tandem system that can achieve spontaneous hydrogen evolution; however, the STH efficiency of approximately 0.35% requires improvement, encouraged, in part, by the excellent potential harvesting characteristics of the semiconductor [10]. Although the optimal design for unassisted solar water splitting is controversial, the abundance of metal oxides with suitable bandgap energies and DSSCs constructed from inexpensive TiO_2 semiconductor/dyes have led to these devices being widely promoted as some of the most promising device configurations for unassisted solar water splitting.

Recently, $BiVO_4$ has attracted great interest as a photoactive material because it has a relatively small bandgap energy and strong light absorption properties for application to PEC water splitting [11–14]. Despite the advantages, $BiVO_4$ itself poses tremendous challenges associated with poor electron transport and a short hole diffusion length. The potentially promising use of type-II WO_3/$BiVO_4$ heterojunction electrodes greatly compromises the poor electrical properties of $BiVO_4$ and poor potential harvesting characteristics of WO_3, limiting the increase in STH conversion efficiency [15–18]. While there are many reports of WO_3/$BiVO_4$ heterojunction PEC cells using film, nanoparticle, nanowire or 3D porous WO_3 as host materials for the guest material ($BiVO_4$) [16–19], studies of WO_3/$BiVO_4$ heterojunction-based tandem devices have been limited, possibly due to the unsatisfactory transparency of the heterojunction structure compared with that of the single semiconductor. Because the solar cells behind a photoanode in the tandem cells must receive more photon energy, heterojunction photoanodes with both high photocurrent density at low bias potential and high transparency for conferring photons to the rear solar cells must be designed.

In this study, we present a facile approach to fabricate a uniform, highly transparent WO_3/$BiVO_4$ photoanode. The proposed bulk-heterojunction-like nanostructure maintains good electron transport ability after coating of the mesoporous WO_3 nanoparticle network with a thin $BiVO_4$ layer. This core/shell structure provides a larger contact area between the WO_3 and $BiVO_4$ components. This structure also provides effective migration of excited electrons from $BiVO_4$ to WO_3 and reduces the thickness of the heterojunction compared with the conventional bilayered structure reported previously [15,16]. The transparency and other optical properties of the fabricated WO_3/$BiVO_4$/DSSC tandem cell were characterised in detail. As the rear DSSCs, high potential cells with a cobalt complex redox shuttle in combination with a porphyrin dye (named JK-306) enabled highly efficient unassisted PEC water splitting beyond 5.7%. This efficiency is the highest value reported thus far.

Experimental section

In this study, we selected the tandem cell configuration described previously [10] and shown in Figure 1, along with the scheme of the band diagram for the whole system. Once light is incident to the high transparent photoanode, the electrons will be excited from valence band to conduction band, which will be transferred to the back side of Pt counter of DSSC. The remained holes oxidise OH^- to oxygen. The transferred electrons are used to reduce $(Co(bpy)_3)^{2+/3+}$ in the DSSC electrolyte (which will return to reduce the LUMO status dye mentioned below to HOMO status). Long wavelength light not absorbed by the photoanode could penetrate the photoanode and reach the anode of the DSSC, where the electrons in the dye molecules on the DSSC anode are excited from the