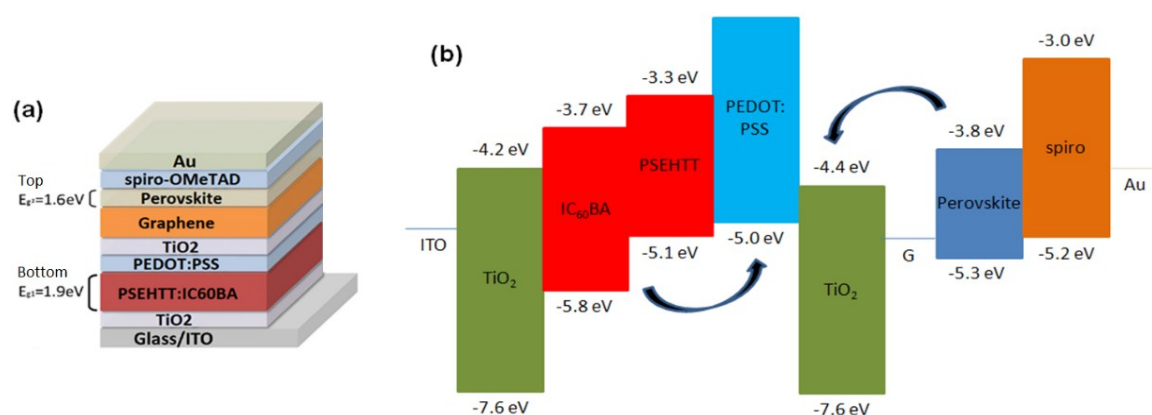


## Supporting Information

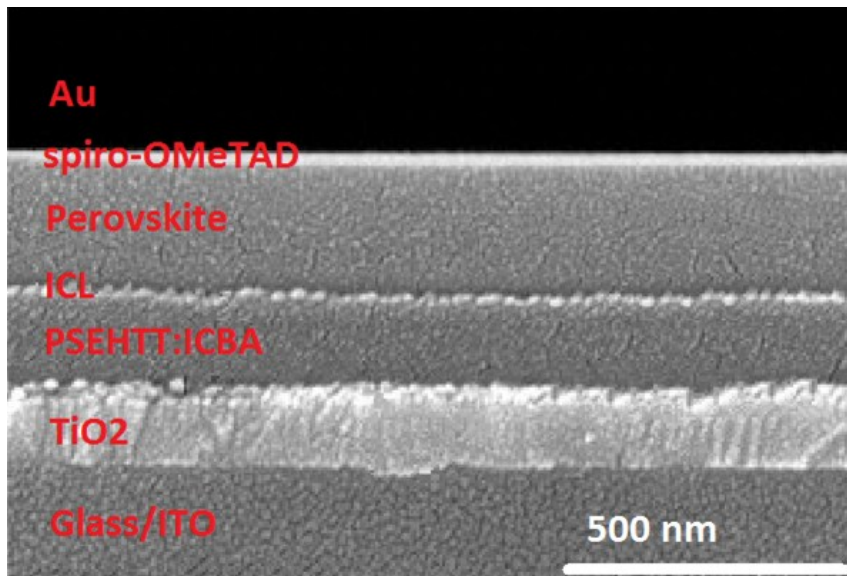
# Highly Efficient Photoelectrochemical Water Splitting by a Hybrid Tandem Perovskite Solar Cell

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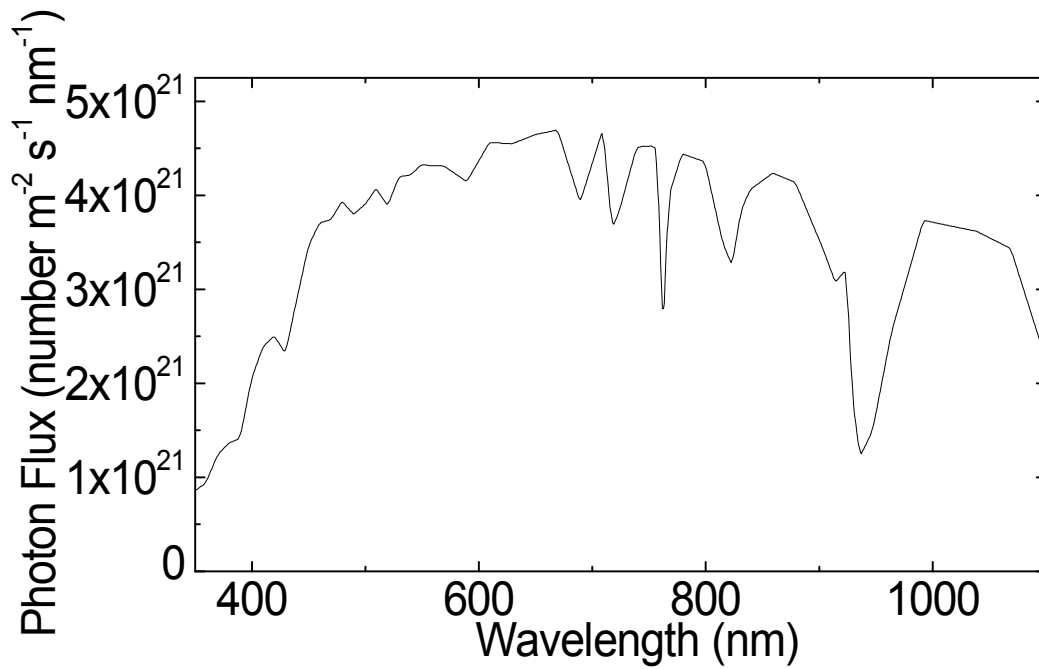
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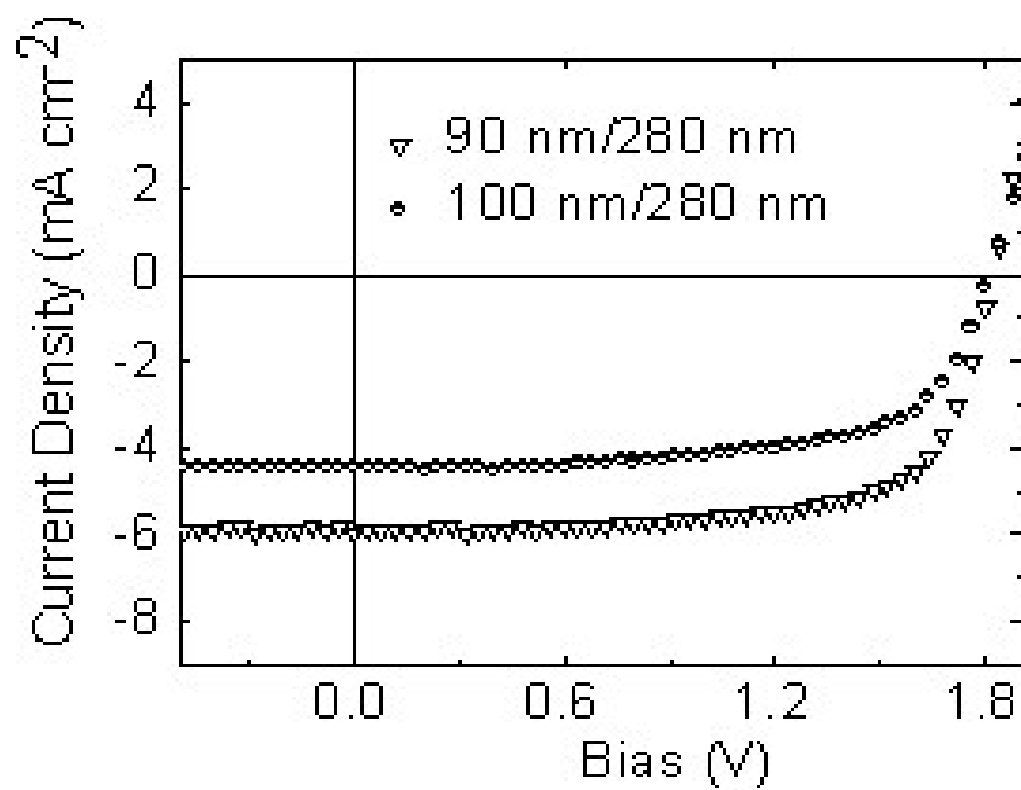
**Figure S1.** Structure, energy-level alignment and efficiency measurements. **a**, Layer stacks of the hybrid tandem perovskite solar cell in an inverted architecture. **b**, Energy levels of the materials investigated in this study.



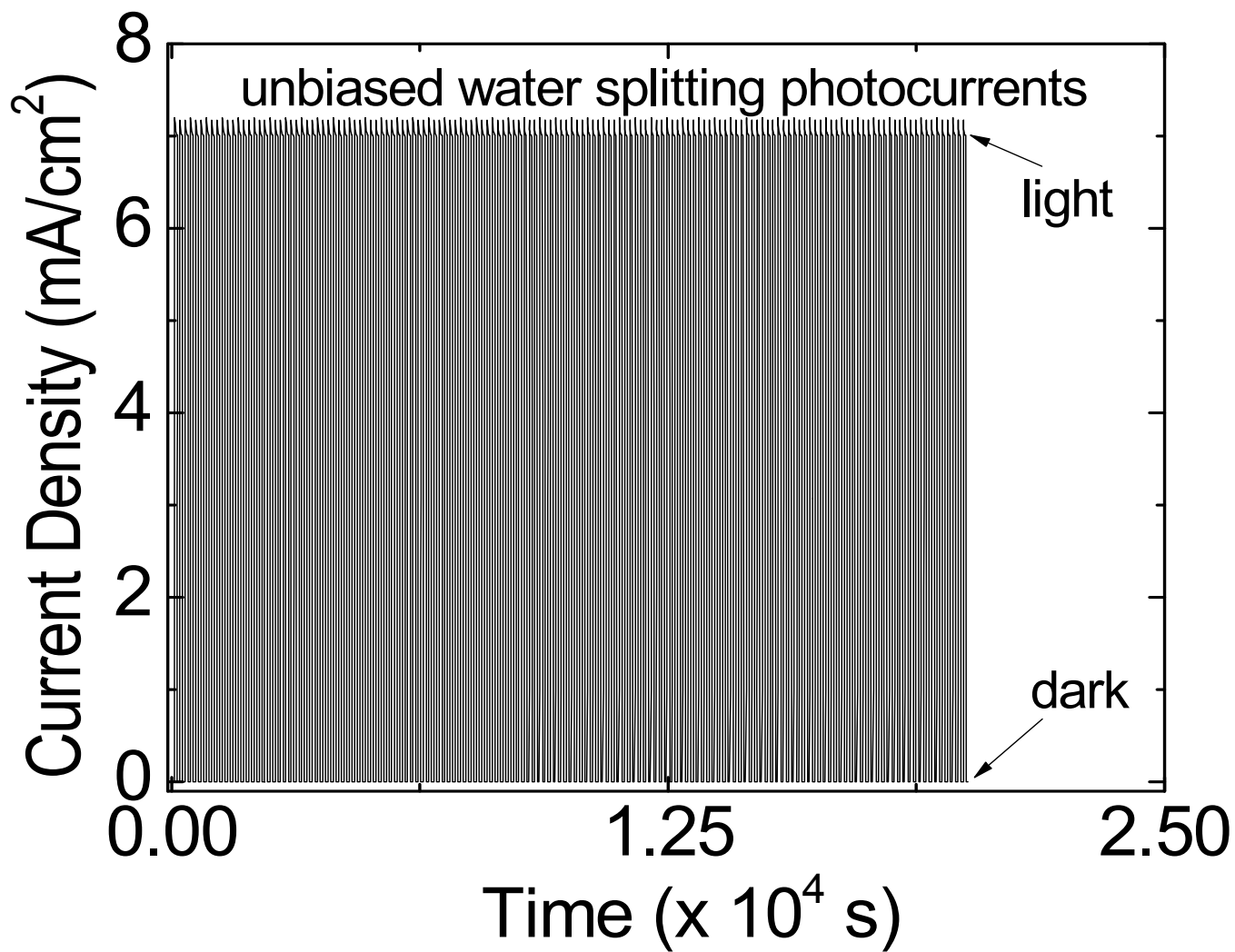
**Figure S2.** Cross-sectional scanning electron microscope of hybrid tandem perovskite solar cells.



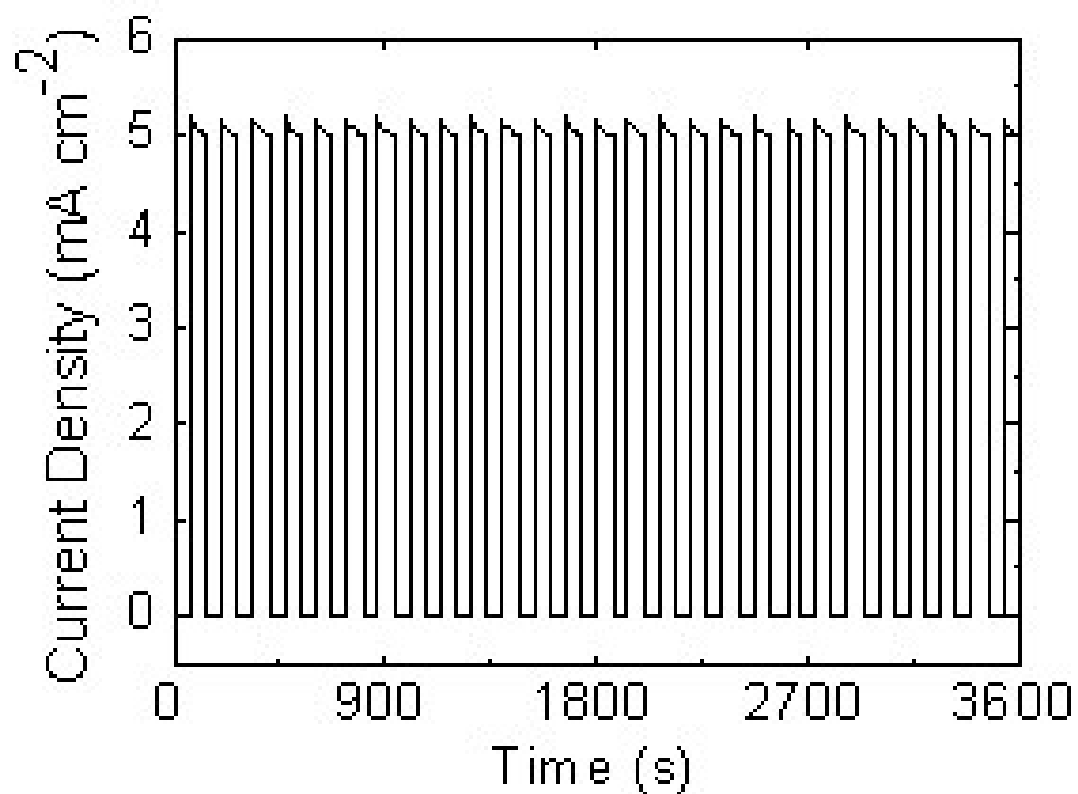
**Figure S3.** The solar radiation spectrum of the light source used in this study.



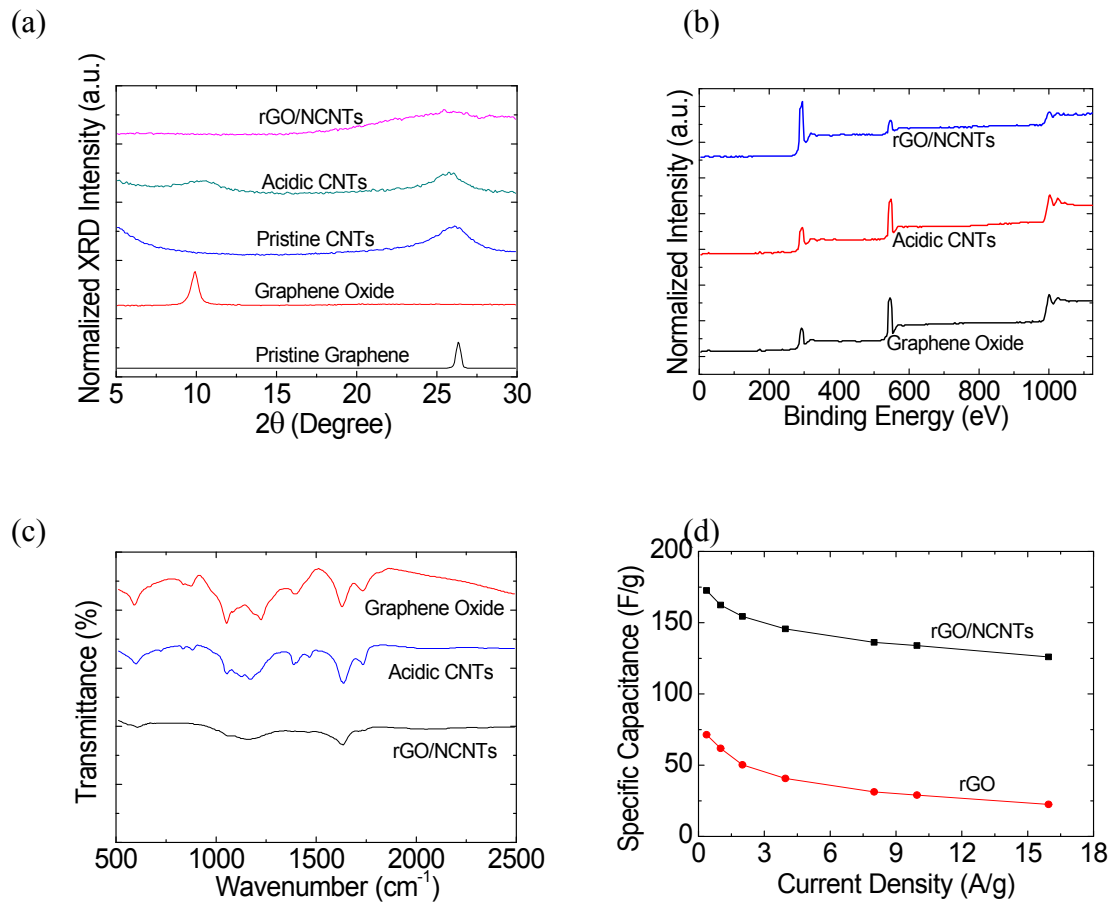
**Figure S4.** Current density curves of hybrid perovskite solar cells with different thickness of the bottom subcell and 280 nm top subcell.



**Figure S5.** Current density-time curve of the integrated PEC water splitting without external bias under chopped simulated AM 1.5G 100 mW cm<sup>-2</sup> illumination.



**Figure S6.** Current density versus time of the photoelectrochemical water splitting without external bias under chopped simulated AM 1.5G 100 mW cm<sup>-2</sup> illumination for 1 h.



**Figure S7.** (a) XRD patterns of the pristine graphene, graphene oxide, pristine CNTs, acidic CNTs and rGO/NCNTs hybrid thin film, (b) FT-IR spectra of the rGO/NCNTs hybrid thin film, acidic CNTs, and graphene oxide, (c) full-scale XPS spectra of the rGO/NCNTs hybrid thin film, acidic CNTs, and graphene oxide, and (d) the rate capabilities of the rGO thin film and rGO/NCNTs hybrid thin film.

**Materials and Methods:** Graphite powder was purchased from Alfa Aesar. 5-aminotetrazole monohydrate (AM) was bought from sigma Aldrich Chemical Reagent CO. Ltd. Other chemicals such as H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, KOH and anhydrous ethanol were bought from Nanjing Chemical Reagent CO. Ltd. The GO was prepared according to modified Hummer's method (25). All solutions used in the electrochemical experiments were freshly prepared with Millipore water having a resistivity of 18.2 MΩ.

The Pt/C sample (20 wt%) was received from Columbia Chemical Company. All other chemicals of analytical grade or better were purchased from Aldrich-Sigma or Fisher Scientific and were used as received. All gases were purchased from Valley National Gases.

The MWCNTs used in this study are commercially available and were purchased from Nanostructured & Amorphous Materials (1240XH, 95%, outer diameter 20–30 nm).

#### Synthesis of N-RGO nanosheets

The synthesis of NrGO nanosheets was followed from the previously published work<sup>(26)</sup>.

#### Preparation of N-CNTs

The preparation of NCNTs was prepared as previously published work<sup>(27)</sup>.

#### Gas measurements

Gas evolution was measured by gas chromatography (SP-6890, nitrogen as a carrier gas) with thermal conductivity detection (TCD).

#### Cyclic voltametry measurements

All of the following electrochemical experiments were performed as described elsewhere<sup>(11)</sup>.

#### Fabrication of hybrid electrocatalyst

Prior to use, glassy carbon electrodes (GCE), 3 mm in diameter, was polished with 0.3 and 0.05 μm gamma alumina slurry, respectively, until a mirror finish was obtained and then ultrasonicated in ethanol and deionized water several times to remove any alumina residue and finally dried in vacuum. Then 4 mg as-prepared N-RGO and N-CNTs were dispersed in 400 μL ethanol-water solution (volume ratio of ethanol to water is 1:1), and ultrasonicated for 30 min to form a homogeneous ink followed by dropping 5 μL suspension onto a GCE substrate (loading: 0.17 mg cm<sup>-2</sup>). After solvent evaporation, the deposited catalyst was covered with 5 μL Nafion solutions (0.5% in ethanol) in order to fix the catalyst on the GCE surface and the prepared electrodes were allowed to dry in air.

#### TiO<sub>2</sub> preparation

Titanium dioxide solution was prepared according to the previously published work<sup>(28)</sup>.

#### Polymer solar cell fabrication

Solar cells were fabricated by first spin-coating a TiO<sub>2</sub> buffer layer on top of pre-cleaned ITO-coated glass substrate (10 Ω/sq. Sunic) at 3500 rpm for 40s and annealed at 150 °C for 10 min under vacuum. The active layer was spin-coated on top of TiO<sub>2</sub> in the glove box. The active layer was spin-coated from a hot solution in a mixed solvent of 1,2-dichlorobenzene (ODCB)



and 1,8-octanedithiol (ODCB:ODT=100:2.5 v/v) at 100 °C and dried in vacuum for 1 h. Next, a PEDOT:PSS (Clevios TM P VP Al 4083, H.C. Stark) buffer layer on top of active layer at 3500 rpm for 40 s and annealed at 150 °C for 10 min under vacuum. Finally, the device was finished by the deposition of 100 nm aluminum, in a thermal evaporator in a vacuum of  $8 \times 10^{-7}$  Torr.

#### Perovskite solar cell fabrication

ITO glass (Sigma Aldrich) was cleaned in an ultrasonic bath containing ethanol for 30 min and the treated in UV/ozone for 30 min. The G-TiO<sub>2</sub> blocking layer (BL) was spin-coated onto ITO at 2000 rpm for 60s, followed by heating at 150 °C for 5 min. The perovskite layer was spin-coated at 2000 rpm for 60s on a warmed substrate from a 40 wt% DMF solution of methylammonium iodide and PbCl<sub>2</sub> (3:1 molar ratio) which formed the perovskite after heating to 100 °C for 45 min. The hole transport layer was spin-coated from an 8.5 wt% of (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-MeOTAD) solution was spin-coated on the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite layer at 4000 rpm for 30s. Finally, 80 nm of gold was thermally evaporated on the spiro-MeOTAD coated film.

#### Tandem solar cell fabrication

The same procedure as that for fabrication of PSEHTT:IC<sub>60</sub>BA as the bottom cell was followed. After depositing the 40 nm PEDOT:PSS and 30 nm TiO<sub>2</sub> layers, the same procedure for fabrication of perovskite as the top cell was followed.

#### Solar cell characterization

During the measurements and stability tests, a shadow mask (0.1 cm<sup>2</sup>) with a single aperture was placed onto the tandem solar cells in order to define its active area. The current density–voltage (J–V) characteristics were recorded with a Keithley 2410 source unit under a solar simulator (AM1.5) with an irradiation intensity of 100 mW/cm<sup>2</sup>. The EQE measurements were performed using EQE system (Model 74000) obtained from Newport Oriel Instruments USA and HAMAMATSU calibrated silicon cell photodiode used as a reference diode. The wavelength was controlled with a monochromator 200-1600 nm.

#### **References**

- (1) Fujishima, K. Honda, *Nature* **1972**, 238, 37.
- (2) T. Saga, *NPG Asia Mater.* **2012**, 2, 96.
- (3) M. Grätzel, *Nature* **2001**, 414, 338.
- (4) [http://www.dyesol.com/media/wysiwyg/Documents/2015-asx-announcements/2015-12-08-DYE0397\\_-\\_EPFL\\_achieves\\_21\\_efficiency.pdf](http://www.dyesol.com/media/wysiwyg/Documents/2015-asx-announcements/2015-12-08-DYE0397_-_EPFL_achieves_21_efficiency.pdf)
- (5) N. S. Lewis, *Science* **2007**, 315, 798.
- (6) C. A. Wolden, J. Kurtin, J. B. Baxter, I. Repins, S. E. Shaheen, J. T. Torvik, A. A. Rockett, V. M. Fthenakis and W. S. Aydil, *J. Vac. Sci. Technol. A* **2011**, 29, 030801.
- (7) A. R. B. M. Yusoff, D. Kim H. P. Kim, F. K. Schneider, W. J. da Silva and J. Jang, *Energy Environ. Sci.* **2015**, 8, 303.
- (8) A. R. B. M. Yusoff, S. J. Lee, H. P. Kim, F. K. Schneider, W. J. da Silva and J. Jang, *Adv. Funct. Mater.* **2014**, 24, 2240.
- (9) S. Esiner, H. van Eersel, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.* **2013**, 25, 2932.
- (10) T. Hamann, *Science* **2014**, 345, 1566.
- (11) J. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. –G. Park, S. D. Tilley, H. J. Fan and M. Grätzel, *Science* **2014**, 345, 1593.

- (12) M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446.
- (13) E. Edri, S. Kirmayer, M. Kulbak, G. Hodes and D. Cahen, *J. Phys. Chem. Lett.* **2014**, *5*, 429.
- (14) E. Edri, S. Kirmayer, D. Cahen and G. Hodes, *J. Phys. Chem. Lett.* **2013**, *4*, 897.
- (15) S. Ryu, J. H. Noh, N. J. Jeon, Y. C. Kim, W. S. yang, J. Seo and S. I. Seok, *Energy Environ. Sci.* **2014**, *7*, 2614.
- (16) S. Subramaniyan, H. Xin, F. S. Kim, S. Shoaee, J. R. Durrant and S. A. Jenekhe, *Adv. Energy Mater.* **2011**, *1*, 854.
- (17) Y. He, H. -Y. Chen, J. Hou and Y. Li, *J. Am. Chem. Soc.* **2010**, *132*, 1377.
- (18) Y. Yuan, *Green* **2011**, *1*, 65.
- (19) S. W. Lee, C. Carlton, N. Risch, Y. Surendranath, S. Chen, S. Furutsuki, A. Yamada, D. G. Nocera and Y. -S. Horn, *J. Am. Chem. Soc.* **2012**, *134*, 16959.
- (20) J. Christensen, P. Albertus, R. S. S. Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed and A. Kojic, *J. Electrochem. Soc.* **2012**, *159*, R1.
- (21) V. Nikolova, P. Illiev, K. Petrov, T. Vitanov, E. Zhecheva, R. Stoyanova, I. valov and D. Stoychev, *J. Power Sources* **2008**, *185*, 727.
- (22) W. -F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. Zhu and R. R. Adzic, *Angew. Chem. Int. Ed.* **2012**, *51*, 6131.
- (23) W. -F. Chen, C. -H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu and R. R. Adzic, *Energy Environ. Sci.* **2013**, *6*, 943.
- (24) J. Perez, E. R. Gonzalez and H. M. Villullas, *J. Phys. Chem. B* **1998**, *102*, 10931.
- (25) Z. Yang, M. Liu, C. Zhang, W. W. Tjiu, T. Liu and H. Peng, *Angew. Chem. Int. Ed.* **2013**, *52*, 3996.
- (26) Z. -J. Lu, S. K. Katla, C. Kumara, S. Chattopadhyay, T. Shibata, A. Dass and C. S. S. R. Kumar, *RSC Advances* **2013**, *3*, 3990.
- (27) Y. Tang, B. I. Allen, D. R. Kauffman and A. Star, *J. Am. Chem. Soc.* **2009**, *131*, 13200.
- (28) A. Hadipour, R. Müller and P. Heremans, *Org. Electron.* **2013**, *14*, 2379.