Efficient direct solar-to-hydrogen conversion by *in situ* interface transformation of a tandem structure

Matthias M. May¹²³, Hans-Joachim Lewerenz⁴, David Lackner⁵, Frank Dimroth⁵ & Thomas Hannappel²

Photosynthesis is nature’s route to convert intermittent solar irradiation into storable energy, while its use for an industrial energy supply is impaired by low efficiency. Artificial photosynthesis provides a promising alternative for efficient robust carbon-neutral renewable energy generation. The approach of direct hydrogen generation by photoelectrochemical water splitting utilizes customized tandem absorber structures to mimic the Z-scheme of natural photosynthesis. Here a combined chemical surface transformation of a tandem structure and catalyst deposition at ambient temperature yields photocurrents approaching the theoretical limit of the absorber and results in a solar-to-hydrogen efficiency of 14%. The potentiostatically assisted photoelectrode efficiency is 17%. Present benchmarks for integrated systems are clearly exceeded. Details of the *in situ* interface transformation, the electronic improvement and chemical passivation are presented. The surface functionalization procedure is widely applicable and can be precisely controlled, allowing further developments of high-efficiency robust hydrogen generators.

¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Solar Fuels, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany. ²Department of Physcis, Technische Universität Ilmenau, Gustav-Kirchhoff-Str. 5, D-98693 Ilmenau, Germany. ³Department of Physcis, Humboldt-Universität zu Berlin, Newtonstraβe 15, D-12489 Berlin, Germany. ⁴California Institute of Technology, Joint Center for Artificial Photosynthesis, 1200 East California Boulevard, Pasadena, California 91125, USA. ⁵Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstraße 2, D-79110 Freiburg, Germany. Correspondence and requests for materials should be addressed to H.J.L. (email: lewerenz@caltech.edu) or to T.H. (email: thomas.hannappel@tu-ilmenau.de).
Hydrogen provides the highest energy density among the common fuels. In the search for sustainable, low-carbon replacements for fossil fuels, solar water splitting is receiving exceptional attention, with H₂ as the crucial ingredient of an anthropogenic carbon cycle or a completely carbon-free energy economy. Solar energy is stored in chemical bonds by splitting H₂O photoelectrochemically into H₂ and O₂. The associated thermodynamic potential difference of 1.23 V must be exceeded by the free energy of the charge carriers transferred to the electrolyte. The required, minimum photovoltage for the photolysis of water is ≥1.6 V, including catalyst overpotentials, and depends on the chosen photocurrent density. Since excess energy is dissipated as heat, the chemical energy stored in a single H₂ molecule is 2 x 1.23 eV. Overcoming the voltage threshold and utilizing a constant energy per reduced hydronium ion requires photocurrent maximization, if the photovoltaic suffices to drive the reaction. These boundary conditions make tandem photovoltaic devices, where semiconductor absorber layers with different energy gaps are combined for enhanced exploitation of the solar spectrum, superior candidates for photoelectrochemical water splitting. As a highly efficient, inorganic analogue to the Z-scheme of natural photosynthesis, dual-tandem structures water splitting. As a highly efficient, inorganic analogue to the Z-scheme of natural photosynthesis, dual-tandem structures are envisaged for enhanced exploitation of the sunlight efficiently, thus permitting high photocurrents. Despite employing relatively high-cost, photovoltage and delivered power at the expense of the energetic situation near the maximum power point of the device, where, for high fill factors, the photovoltage is close to the OC voltage, but the photocurrent is still near its maximum (short circuit) value. The photovoltage generated is represented by the

**Results**

**Customized tandem absorber.** A two-junction tandem absorber structure, grown epitaxially on a Ge substrate by metal-organic vapour phase epitaxy, serves as photovoltaic core element. The absorber consists of a GaInP / GaAs bottom cell with an energy gap of Eₜ₂ = 1.78 eV and of an n-i-p GaInAs bottom cell with Eᵣ₁ = 1.26 eV (Fig. 1a). The structure also contains cap layers and an AlInP window layer for electron collection. In the photovoltaic mode and with anti-reflection coating, a short-circuit current density of up to 15 mA cm⁻² and an open-circuit (OC) voltage of 2.1 V is expected at AM 1.5G illumination. The energy band relations are depicted in Fig. 2. They show the energetic situation near the maximum power point of the device, where, for high fill factors, the photovoltage is close to the OC voltage, but the photocurrent is still near its maximum (short circuit) value. The photovoltage generated is represented by the

**Figure 1 | Interfacial functionalization steps.** The tandem consists of a GaInP / GaAs top cell and a GaInAs n-i-p bottom cell. (a) Stacking and thicknesses; t₁ and t₂, and Ω denote tunnel junctions and ohmic back contact, respectively; vertical arrows indicate selective chemical etching of the capping layer. (b) Chemical and photoelectrochemical surface transformation of the AlInP window layer in an aqueous solution of RhCl₃. (c) Electrochemical deposition of a seed layer of Rh electrocatalysts (grey) and photoelectrodeposition of a continuous electrocatalyst film (red; see text). (d) Oscillation of the open-circuit potential on illumination during functionalization. (e) Transmission electron microscope image of a cross-section of the surface after Rh catalyst deposition; scale bar, 10 nm.
difference of the quasi-Fermi levels of electrons (blue curve in Fig. 2) and holes (red curve), yielding the achievable free energy of the system near the maximum power point. The structure operates as photocathode with a dark anode using a RuO₂ catalyst for O₂ evolution.

Interface functionalization. The fundamental surface processing steps are summarized in Fig. 1a–c. A protective cap layer was removed by selective etching in a solution of NH₄OH:H₂O₂:H₂O, stopping at the n⁺-doped Al₀.₃₅In₀.₆₅P window layer. A suitable surface for the subsequent functionalization was prepared by chemical oxidation in O₂-saturated water, followed by a drying process in a flow of oxygen, resulting in a smooth, oxidized surface. The surface composition was analysed by X-ray photoelectron spectroscopy (XPS), revealing a mixed In/Al oxide layer on top of the AlInP window (Fig. 3). Such oxide layers typically form a barrier for holes, reducing charge-carrier recombination.

Combined chemical and photoelectrochemical surface conditioning is essential to increase stability and charge transfer efficiency, as the stability of a chemically formed, pure group III element (In and Al) oxide layer, which is the outcome of the etching process (Figs 1a and 3), can be rather limited under operating conditions. We developed an advanced, but straightforward procedure that allows for simultaneous surface functionalization and catalyst deposition in a single solution in a two-step approach (Fig. 1b–d). In situ process, the method also prevents unfavourable oxidation from ambient O₂ (ref. 22). Under OC conditions, the sample was illuminated with white light, initiating an oscillation (Fig. 1d) of the observed potential. Oscillation periods were in the range of 20 s with amplitudes in the order of 100 mV. After typically 5–6 oscillations, the OC potential reached its maximum. We attribute this phenomenon to a slow layer-by-layer etching, where surfaces with superior electronic quality are simultaneously prepared. The process shows similarity to the current-oscillations observed at the Si—electrolyte contact, in this model, the anodic and the cathodic currents equilibrate at OC; the anodic partial current leads to oxide formation in competition with the cathodic processes of H₂ evolution, excess minority carrier recombination, and the reduction of formed oxides. Oscillations occur if, within one cycle, the locally formed initial oxide islands are reduced more slowly, hence are more stable than the later formed ones, which exhibit more strain-induced defects. This constitutes a feedback mechanism that synchronises the oxidation and the cathodic etching process. This hypothesis is supported by the finding that at the OCP maximum, the thickness of the oxide is reduced to 0.4 nm, in comparison with 0.8 nm at the OCP minimum (Supplementary Fig. 1). Analogous formation of intermediate islands, mediated by surface defects, has also been observed for the removal of oxides from III–V surfaces in gasphase experiments. The periodic change of the photovoltage is attributed to periodic thickness variations, corresponding potential drops across the interfacial film, and periodically increased recombination within a cycle when more defect-rich films are formed. The photovoltage is highest for the least oxidized surface.

The photovoltage oscillation step was directly followed by electrodeposition of the Rh electrocatalyst. The deposition was performed by applying potential pulses of 50 ms duration over a time of typically 30 s in the dark (see the Methods section). Subsequently, photofunctionalization of Rh was carried out by periodically varied illumination between low and high light intensity, followed by 30 s in the dark (Supplementary Fig. 2). The oscillating behaviour of the OCP on illumination during the functionalization is not a unique feature of the Rh-containing interface, however, the beneficial effect of the oscillation on the surface is maximized if the catalyst deposition is conducted directly thereafter, that is, in the same electrolyte.

The process resulted in a composite structure of seed catalyst nanoparticles and a thin Rh covering layer (Fig. 1c,e). XPS
revealed that the initial surface functionalization before Rh deposition led to a reduction of the In content at the surface and, preferentially, of the relative In oxide contribution (Fig. 3a). While the Al 2s line (Fig. 3b) is slightly reduced and develops a small shoulder towards higher binding energies, the P 2p signal shows a partial transformation into a mixture of InPO₄ and In₃(PO₄)₂, indicated by the peak between 133 and 134 eV binding energy. Peak analysis shows that the relative PO₄ contribution is increased from initially 6 to 67% after functionalization.

Photoemission lines of the functionalised surfaces are, compared with those of the etched samples, shifted by (0.75 ± 0.1) eV to higher binding energies (Fig. 3). This shift originates in part from the higher n-doping of the functionalised, phosphate- and phosphite-rich surface, also observed for InP photocathodes.

For the oxidized sample directly after etching, the Fermi level at the topmost surface is energetically lowered in comparison with the highly n-doped AllnP bulk due to a lower doping and a higher electron affinity of the oxide. The completely functionalised surface that was transformed towards PO₄ on the other hand, exhibits a higher n-doping and the Fermi level is shifted towards the vacuum level (cf. Fig. 3 and Supplementary Fig. 3), improving the band alignment to the AllnP. The beneficial effect of the PO₄ phase is further supported by the observation that the signal strength of this species (Fig. 3b) is directly correlated with the overall efficiency. In a quantitative analysis of the P 2p lines, the average thickness of the phosphate and phosphite layer was estimated to be (1.3 ± 0.2) nm.

An analysis of transient photovoltages (Supplementary Fig. 4) shows an overshoot for not fully transformed surfaces, which indicates a trapping of charge carriers in surface states. Together with the finding, that OC voltages increase significantly for devices with PO₄ termination (cf. Supplementary Fig. 5), we conclude that the functionalization layer also provides an electronic surface passivation. This transformation is a feature of the in situ functionalization before catalyst deposition, which avoids the formation of charge-carrier recombination centres at strained In/Al–O–In/Al bonds, that would form upon exposure to atmospheric O₂.

Cell performance. The output characteristics of the resulting devices (stacking and energy schematic sketched in Figs 1 and 2) were evaluated in 1M HClO₄ under simulated sunlight (AM 1.5G, light intensity I = 100 mW cm⁻²; Fig. 4). Both, results of a two-electrode and a three-electrode potentiostatic measurement are shown. For the former, a current density of j = 11.5 mA cm⁻² without bias is reached, as seen in the inset. With the definition of the solar-to-hydrogen efficiency, η = (j_{OC} × 1.23 V)/I, this translates into an efficiency of η = 14% under the assumption of 100% Faradaic efficiency. A saturation current density beyond 14 mA cm⁻², measured in a three-electrode set-up, is close to its maximum value, indicating that light transmission through the catalyst is not a major issue. The OC potential of 1.9 V is, however, 200 mV below the expected value, which is mainly ascribed to interfacial charge-carrier recombination. In conjunction with the linear exponential catalyst characteristic, this results in the S-shaped onset of the photocurrent. The difference between two- and three-electrode set-up measurements is attributed to the overpotential of the oxygen evolution reaction as well as the solution resistance. The observation of 14 mA cm⁻² at +1.23 V versus RHE results in an assisted photocathode efficiency of >17% for the three-electrode arrangement (blue curve in Fig. 4), demonstrating the potential efficiency of the device. An example for an incomplete functionalization towards PO₄ is given in the Supplementary Fig. 5, showing a significantly reduced fill factor. A successful surface transformation combined, however, with catalyst overloading results in reduced optical transmission and an associated reduction of the photocurrent, while the OC voltage is increased. A total of 8% of the samples, which had an active surface area between 30 and 100 mm², showed highly successful functionalization with photocurrent densities of 11 mA cm⁻² and beyond, 25% exceeded 10 mA cm⁻² (see also the Methods section).

Chronoamperometric data over 40 h are displayed in Fig. 5. For a vertical configuration, the photocurrent density degrades continuously, saturating at 0.5 of its original value after 35 h of operation. Optical inspection of the electrode surface shows that steps in the decrease of the current are associated with severe detachment of catalysts from the surface, likely a result of
chemical etching and stress from H₂ bubbles propagating parallel to the surface, as already proposed in ref. 14. In a horizontal set-up (with slight catalyst overloading as indicated by only \( j = 10 \text{ mA cm}^{-2} \)), no degradation of the photocurrent for over 16 h of operation is noted (see inset of Fig. 4).

These data show the hitherto best stability reported for a monolithically integrated, high efficiency, fully immersed device. Longer stability, obtained with half cells 23,34, cannot directly be compared with those of tandem structures because the absorbers used in those experiments were high-quality single-crystalline Si, GaAs, InP and GaP. In heteroepitaxy for tandem cells, multi-stack layer growth results in growth-induced defects that can protrude to the surface. Such sites can act as nucleation centres for subsequent defects, which develop during surface transformation, electrodeposition and finally operation. Resulting pinhole formation leads to a reduced mechanical stability of the Rh catalyst due to undercutting at sites, where the corrosion protection layer has been incompletely formed. The mechanical detachment of the catalyst is more severe in a vertical configuration of the electrode, where gas bubbles, which have been observed to move directly along the surface, induce optical and mechanical interaction in particular at defect sites and further local corrosion. Our results point to the necessity to prepare custom-designed tandem absorber structures because the difference in surface chemistry at defect sites will also limit protection possibilities via atomic layer deposition. A possible solution could be the deposition of thin layers of earth-abundant materials by physical vapour deposition followed by under potential deposition 35 of the catalyst, which would also reduce the overall noble-metal consumption.

High Faradaic solar-to-hydrogen efficiency is confirmed by the measurement of gas evolution (Fig. 6a), exhibiting a 2:1 ratio of H₂ to O₂ and an equivalent of the evolved gases to the overall charge transferred within the measurement error of ca. 5%.

To estimate the Faradaic efficiency, we consider a potential lateral removal of the flat, epitaxial absorber structure (0.8 µm for the top cell). In a cathodic corrosion process, where PH₃ is formed, three electrons are liberated per Al/In atom 26, which is equivalent to 12 electrons per crystal unit cell. With a lattice constant \( a = 0.57 \text{ nm} \), this translates into a charge of 1.04 mC cm⁻² for the corrosion of 1 nm. Assuming a (conservative) average current density of 7 mA cm⁻² during the long-term experiment in Fig. 5 over 40 h and homogeneous corrosion, this would result in a removal of 1 nm, if all the current would be due to corrosion. As the device still splits water after 40 h, the corroded thickness is certainly <0.8 µm, the thickness of the top cell. Hence, the lower boundary of the Faradaic efficiency for H₂ evolution can be estimated to be >99.9%. Gas measurements (Fig. 6a) confirm such a high Faradaic efficiency with the ratio of cathodic to anodic products of 2:1 and the overall amount of gases very close to the expected value derived from the integration of the current.

A general motif of a successful functionalization of InP-based surfaces appears to be the formation of phosphate and phosphite species, simultaneously providing stability as well as efficient charge transfer 22,23. For the AllnP surface studied here, the removal of mixed Al/In oxides and the concurrent incorporation of oxygen in the form of PO x on the first 1–2 nm is a crucial prerequisite for stability and efficiency. While In–O–In bonds were indeed predicted to form potential charge-carrier recombination centres 24, the phosphate species seem to provide a similar surface passivation as it was observed in the case of cobalt phosphate on metal-oxide electrodes 36.

For an energetic consideration of the interface formation during functionalization, two junctions have to be regarded, the buried solid–solid interface between the pure, as-grown, AllnP window layer and its oxygen-containing surface layer, as well as the solid–liquid interface between this oxygen-modified surface layer and the electrolyte. In the case of the buried junction, the electron affinities, \( \chi \), of the AllnP and the oxide/PO x species have to be considered. While AllnP exhibits \( \chi = 3.8 \text{ eV} \) (ref. 18), it changes to \( \gamma \approx 4.4 \text{ eV} \) for indium oxide 31. Such differences in electron affinity between III–V semiconductors and their oxides with their potential impact on the photovoltage have already been addressed in the literature 37. The transformation of the surface layer towards a POₓ-rich phase with its reduced electron affinity 38 does, however, shift the conduction band back towards the vacuum level, reducing the band offset at the buried junction. This is supported by XPS, showing a binding energy of the In 3d peak of 443.8, 444.2 and 444.6 eV for the freshly etched, the partly functionalised and the fully functionalised surface, respectively. This trend is confirmed by Mott–Schottky analysis, where the flat band of −0.7 V versus RHE for the fully functionalised surface corresponds to 3.9 eV versus the vacuum level, which is very close to what is expected for n-doped AllnP.

Due to the high n-doping in the AllnP and the ultrathin (<2 nm) oxide/PO x layer, the junction between the absorber surface and the Rh nanoparticles is mainly defined by the Fermi level of the semiconductor 39, and space charge regions are expected to be thin enough for tunnelling. Consequently, the reduction of the surface recombination velocity by the POₓ-rich phase is the main beneficial effect of the surface functionalization.

Our findings suggest that the functionalization should be transferable to other PV-based III–V (tandem) absorbers, which exhibit an InP-containing top layer or an In-rich compound surface. In cases where the absorber does initially not exhibit such a top layer, it is possible to terminate absorber growth with a thin, not necessarily lattice-matched, InP layer on top. As the functionalization mainly depends on the surface chemistry and the Fermi level at the surface (which can be tuned by doping), the
InP layer could serve as a sacrificial functionalization precursor. Such an approach would consequently widen the material choice for the underlying tandem structure.

With the near-optimum, low light attenuation catalyst loading found here, the amount of Rh for 1 MW electrochemical power output would be in the order of 1 kg. This mass could be considerably reduced by the use of core-shell catalyst nanoparticle preparations, for example, by under potential deposition and galvanic exchange with a core of an earth-abundant material. Further cost reductions from the substrate side could be achieved by the employment of lift-off techniques or the switch to Si substrates, targeting in combination with light concentration the high-efficiency route to low-cost H2 (ref. 7,9).

The results demonstrate that in situ modification of surfaces enables exceptionally high efficiency for unassisted solar water splitting. The combination of (photo)electrochemical functionalization with surface science analyses provides atomic level insights and feedback for the optimization of the charge transfer processes and interfaces. A further improvement of the functionalization-based potential to achieve even higher stability with the need for protective layers by atomic layer deposition, which would introduce additional processing.

If the gap between potential (17.4%) and achieved (14%) solar-to-hydrogen can be further reduced, devices producing solar H2 below 4$/kg9 could become feasible.

Methods

Epitaxial absorber growth and ohmic contact. The tandem absorber was grown epitaxially by metal-organic vapour phase epitaxy on a Ge substrate. The lattice mismatch to the substrate was accounted for by an intermediate step-grading buffer, gradually changing the lattice constant from the substrate to the absorber.

For a detailed description, the reader is referred to ref. 19. The ohmic back contact was prepared by evaporating Ni and Au on the substrate, followed by annealing.

Etching and chemical oxidation. Before etching, samples were cleaned in 2-propanol and water to remove initial surface contamination. The etching procedure removed the cap layer stopping on the AlInP window layer. The etching solution was composed of NH3·H2O (25%, Sigma Aldrich p.a. grade), H2O2 (30%, Merck p.a. grade) and H2O in a ratio of 1:1:10 and prepared directly before the etching. All the H2O was ultrapure ‘Milli-Q’ grade. Immediately after the removal of the window layer, samples were rinsed in H2O, saturated with O2 by purging. The resulting hydrophilic surface was then slowly dried in a stream of O2 for several minutes. Surface transformation was performed in a three-electrode setup consisting of a Pt counter electrode and an Ag/AgCl reference electrode in an aqueous RhCl3 solution. Samples were encapsulated in a two-component epoxy resin or, if XPS analysis was performed, clamped against a sealing ring.

Surface transformation and Rh deposition. The electrolyte for functionalization and Rh deposition was an aqueous solution of 5 mM Rh(III) chloride trihydrate (99.98%, Sigma Aldrich) + 0.5 M KCl (99.5%, Alfa Aesar) + 0.5 vol% 2-propanol (Sigma Aldrich p.a. grade). White light was provided by a tungsten iodide lamp. In the three-electrode setup, the voltage of the working electrode (the sample) is controlled via a potentiostat (PAR Versastat 3) against a reference electrode, in this case Ag/AgCl (+0.197 V versus the normal hydrogen electrode) 41. The current source was used. Due to the high photoactivity of the samples inducing a surface photovoltage, energy calibration was achieved by setting the binding energy (relative to the Fermi level E_F) of the C 1s line to 284.8 eV. Voigt profiles in combination with a linear background were employed for peak analysis.

For the XPS measurements at different stages of the OCP oscillation (Supplementary Fig. 1), the electrochemical experiment was abruptly interrupted and the sample transferred to Ultra-high vacuum (UHV). To rule out a potential build-up of oxide by subsequent interruptions of the electrochemical experiment, the order of the XPS measurement with respect to maximum/minimum was reversed for different samples, confirming the results.

As the reduction of Rh3+ to metallic Rh competes with the H2 evolution reaction, the Faradaic efficiency for the deposition is not unity. This explains the transferred charges in the order of 50 mC cm−1, which would otherwise result in a (closed) Rh layer with a thickness in the order of 10 nm. The optimum catalyst loading exhibits a relatively narrow process window: a larger loading results in a higher OC voltage and a steeper onset of the photocurrent, but this increase is over-compensated by a lower photocurrent due to increased light attenuation by the catalyst.

Output characteristic. The set-up for determination of the output characteristics was again a three-electrode set-up with Pt as counter electrode and Ag/AgCl as reference electrode or a two-electrode set-up with a RuO2 counter electrode (1 cm2). A commercial Wacom WXS-50S solar simulator provided the AM 1.5G spectrum at the location of the sample, which was calibrated quantitatively by a spectrometer, which was acquired using an Ocean Optics USR2000 + RAD spectrometer, to AM 1.5G. The PTFE cell (as described in ref. 42) was equipped with a quartz plate as front window and an O-ring of 6 mm diameter defining the active surface. Electrical connection was assured by a gold finger pressed against the back of the ohmic contact of the solar cell. In the cases, where samples were embedded in epoxy resin, an all-quartz cell was employed. The electrolyte was 1 M HClO4 and, in most cases for the vertical configuration, 1 mM Triton X 100 as a surfactant to reduce the bubble size. Long-term stability in the horizontal set-up, described in the former paragraph, was evaluated without the use of a surfactant. Eighteen hours into the chopped long-term experiment in Fig. 5, an intermediate failure of the chopper, caused by a musca domestica, lead to constant illumination for 2 h.

Statistics: out of 65 analysed samples, 25% showed current densities beyond 10 mA cm−2 and 8% above 11 mA cm−2.

Galvanic exchange with a core of an earth-abundant material could become feasible.

Photoelectric spectroscopy. For photoelectrochemical experiments, a monochromated Al Kα source was used. Due to the high photoactivity of the samples inducing a surface photovoltage, energy calibration was achieved by setting the binding energy (relative to the Fermi level E_F) of the C 1s line to 284.8 eV. Voigt profiles in combination with a linear background were employed for peak analysis.

The XPS measurements at different stages of the OCP oscillation (Supplementary Fig. 1), the electrochemical experiment was abruptly interrupted over a sample transferred to Ultra-high vacuum (UHV). To rule out a potential build-up of oxide by subsequent interruptions of the electrochemical experiment, the order of the XPS measurement with respect to maximum/minimum was reversed for different samples, confirming the results.

References

1. Parkinson, B. & Turner, J. in Photoelectrochemical Water Splitting: Materials, Processes and Architectures (eds Lewerenz, H.-J. & Peter, L.) Ch. 1, 1–18 (The Royal Society of Chemistry, 2013).

2. Olah, G. A., Prakash, G. K. S. & Goeppert, A. Anthropogenic chemical carbon cycle for a sustainable future. J. Am. Chem. Soc. 133, 12881–12898 (2011).

3. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972).

4. Gerischer, H. Heterogeneous electrochemical systems for solar energy conversion. Pure Appl. Chem. 52, 2649–2667 (1980).

5. Bard, A. J. Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors. J. Photochem. 10, 59–75 (1979).

6. Shockley, W. & Queisser, H. J. Detailed balance limit of efficiency of p–n junction solar cells. J. Appl. Phys. 31, 510–519 (1960).

7. Hannappel, T., May, M. M. & Lewerenz, H.-J. in Photoelectrochemical Water Splitting: Materials, Processes and Architectures (eds Lewerenz, H.-J. & Peter, L.) Ch. 9, 223–265 (The Royal Society of Chemistry, 2013).

8. Würfel, P. & Würfel, U. Physics of Solar Cells: from Basic Principles to Advanced Concepts (John Wiley & Sons, 2009).

9. Pinaud, B. A. et al. Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. Energy Environ. Sci. 6, 1983–2002 (2013).

10. Seger, B. et al. 2-Photon tandem device for water splitting: comparing photocathode first versus photoanode first designs. Energy Environ. Sci. 7, 2397–2413 (2014).

11. Bard, A. J. & Fox, M. A. Artificial photosynthesis: Solar splitting of water to hydrogen and oxygen. Acc. Chem. Res. 28, 141–145 (1995).

12. Licht, S. et al. Over 18% solar energy conversion to generation of hydrogen fuel: theory and experiment for efficient solar water splitting. Int. J. Hydrogen Energy 26, 653–659 (2001).

ARTICLE NATURE COMMUNICATIONS | DOI: 10.1038/ncomms9286

© 2015 Macmillan Publishers Limited. All rights reserved.
13. Luo, J. et al. Water photolysis at 12.3% efficiency via perovskite photocatalysts and earth-abundant catalysts. *Science* **345**, 1593–1596 (2014).

14. Khaselev, O., Przasnyski, M. & Gerischer, H. Underpotential deposition of metals and work function differences. *J. Electroanal. Chem.* **54**, 25–38 (1974).

15. Zhong, D. K., Choi, S. & Gamelin, D. R. Near-complete suppression of surface recombination in solar photoelectrolysers by Co-Pi catalyst-modified W:BiVO₄. *J. Electrochem. Soc.* **165**, 41–59 (2018).

16. Kaiser, B. et al. Solar hydrogen generation with wide-band-gap semiconductors: GaP(100) photoelectrodes and surface modification. *ChemPhysChem* **13**, 3053–3060 (2012).

17. Robach, Y. et al. Passivation of InP using In(PO₃)₃-condensed phosphates: from oxide growth properties to metal-insulator-semiconductor field-effect-transistor devices. *J. Appl. Phys.* **71**, 2981–2992 (1992).

18. Calvet, W. et al. Silicon based tandem cells: novel photocathodes for hydrogen production. *Phys. Chem. Chem. Phys.* **16**, 12034–12050 (2014).

19. Zhong, C. J. & Maye, M. Coreshell assembled nanoparticles as catalysts. *J. Adv. Mater.* **13**, 1507–1511 (2001).

20. Bard, A. J. & Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications* 2nd edn (Wiley, 2001).

21. van de Krol, R. & Grätzel, M. *Photoelectrochemical Hydrogen Production* Vol. 102 (Springer, 2011).

22. King, D. M. & Bard, A. J. Coulometric analysis with gas volume measurement. *Anal. Chem.* **36**, 2351–2352 (1964).

Acknowledgements

We are grateful for support by R. van de Krol and for experimental support by M. Kernbach and H. Kriegel. M. Niemeyer, C. Karcher and J. Ohlmann supported the solar cell development. K. Harbauer and T. Münchenberg assisted with ohmic contact preparation. U. Bloeck performed the TEM measurements, S. Brunken provided the RuO₂ counter electrode. We also thank P. Bogdanoff, K. Fountaine and C. McCrory for helpful discussions. M.M.M. acknowledges a scholarship by the Studienstiftung des deutschen Volkes and H.-J.L. acknowledges support by the DFG (project Nr. 1192-3/4). The discussion and interpretation of the data, feedback with experimentation as well as article layout and writing was also supported by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the US Department of Energy under Award Number DE-SC0004993.

Author contributions

T.H., H.-J.L. and M.M.M. designed the study. M.M.M. executed the experiments and did the data analysis. D.L. and F.D. prepared the tandem absorber. M.M.M. and H.J.L. wrote the paper and all authors commented on the manuscript.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: May, M. et al. Efficient direct solar-to-hydrogen conversion by in situ interface transformation of a tandem structure. Nat. Commun. 6:8286 doi: 10.1038/ncomms9286 (2015).