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Bioinspired molecular co-catalysts bonded to a silicon photocathode for solar hydrogen evolution

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The production of fuels from sunlight represents one of the major challenges to the development of a sustainable energy system [1-5]. Hydrogen is the simplest fuel to produce and while platinum and other noble metals are efficient catalysts for photoelectrochemical hydrogen evolution [6-9], earth-abundant alternatives are needed for large-scale use [10-15]. We show that bioinspired molecular clusters based on molybdenum and sulfur evolve hydrogen at rates comparable to that of platinum [6]. The incomplete cubane-like clusters (Mo_3S_4) efficiently catalyze the evolution of hydrogen when coupled to a *p*-type Si semiconductor that harvests red photons in the solar spectrum. The current densities at the reversible potential match the requirement of a photoelectrochemical hydrogen production system with a solar-to-hydrogen efficiency in excess of 10% [16]. The experimental observations are supported by DFT calculations of the Mo_3S_4 cluster adsorbed on the hydrogen-terminated Si(100) surface providing insights into the nature of the active site.

Ideally, solar fuel production should be linked directly to the harvesting of light [4, 17-19]. The “chemical solar cell” depicted in Fig. 1 shows one possible way to do this in a manner that utilizes a large part of the solar spectrum [4, 19]. The pillared structure ensures an effective harvesting of the photons and an effective photocurrent collection (by virtue of the length available for absorption combined with short, radial, minority

carrier transport distances) while also exposing a large surface area for the catalytic reactions. In the “chemical solar cell” the blue part of the solar spectrum is absorbed by a photoanode, where water is oxidized to release oxygen and protons. The red part of the spectrum, unabsorbed by the large band-gap photoanode, passes through to be absorbed by the photocathode where protons are reduced to evolve hydrogen. The two-photon tandem approach allows access to a larger part of the solar spectrum than single-photon water splitting [8]. Si has a band gap of 1.12 eV and is excellent for capturing photons in the red part of the solar spectrum. Recently, Boettcher *et al.* have shown how to produce pillar-arrays of scalable CVD grown Si [20].

Importantly, assuming that 10% of the energy supplied from the sun at peak intensity (1000 W/m^2) is harvested, the current density will be $\sim 8 \text{ mA/cm}^2$ at both the cathode and the anode (connected in series) [16]. To obtain sufficient efficiency, co-catalysts for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are required in the “chemical solar cell”. Platinum and other noble metals are efficient electrocatalysts for HER [7] but they are too scarce (and expensive) to be used for large scale energy production, and therefore abundant (and inexpensive) alternatives must be developed. Based on the observation that the free energy of hydrogen adsorption, ΔG_{H} , is a good descriptor for identifying HER catalysts [21] and the fact that the transition metal sulfides in nitrogenases [22] and hydrogenases [23] are excellent HER catalysts with close to optimum ΔG_{H} 's, we have previously found that MoS_2 nanoparticles are good catalysts for this reaction [10, 24]. This bio-mimetic approach has been extended to include cubane-type molecular metal-sulfide clusters [25], a building block commonly found in co-factors of enzymes [26-28]. In the following we show that an incomplete cubane-like Mo_3S_4 cluster is an efficient co-catalyst for HER when coupled to *p*-Si photocathodes. Under illumination with the red part of simulated sunlight, the current density reaches 8 mA/cm^2 at the reversible hydrogen evolution potential on the planar Si(100) surface. Further, clusters supported on Si pillars show an enhanced performance with respect to that on planar samples, which is promising for potential application in a “chemical solar cell”.

Four photoelectrodes are compared. Two samples are naked H-terminated Si(100): a planar Si(100) and pillar structured Si(100). The same two surfaces were then modified by the Mo_3S_4 cluster. Molecular Mo_3S_4 clusters are preparatively available with different ligand environments [29]. A Mo_3S_4 cluster with hydrophobic methylcyclopentadienyl ligands was chosen (cluster synthesis and structure see Supplementary Fig. S1) making the cluster insoluble in water but soluble in polar organic solvents. For the preparation of the cluster-modified photoelectrodes, a dichloromethane/methanol solution of the Mo_3S_4 clusters was drop-casted onto H-terminated *p*-Si(100). In the photocatalytic experiments, the photoelectrodes were illuminated by using the

long wavelength ($\lambda > 620$ nm) part of simulated AM 1.5G radiation. In order to get the overall light intensity to approximate the AM 1.5G level in the range of 620 – 1050 nm, the light source was a Xe-arc lamp with suitable filters. The collimated light intensity incident on the Pyrex window of the photoelectrode compartment was measured to be 28.3 mW/cm^2 and the photon flux 1.08×10^{17} photons/(s·cm²) (17.2 mA/cm^2 , see Supplementary Fig. S2). Various amounts of Mo₃S₄ cluster were drop-casted and 2 nmol was found to be optimal. XPS confirmed that the clusters were deposited on the Si surface (see Supplementary Fig. S3). However, subsequent XPS analysis showed that only 2.6×10^{13} Mo₃S₄ clusters/cm² remained on the surface after photochemical test implying that most of the deposited clusters were lost into the electrolyte. Since pulling the sample out of the electrolyte in inert gas does not change the activity, we conclude that this is also the area density of clusters during test.

Fig. 2a shows all the electrochemical and photoelectrochemical data of the four samples. In the dark all electrodes show negligible current. Under illumination the naked planar Si has an onset of photocurrent at $U_{\text{RHE}} = -0.4$ V. Upon depositing the Mo₃S₄ clusters a significant enhancement in photoactivity is observed, with an onset shifted to $U_{\text{RHE}} = +0.15$ V due to improved catalysis. This results in a hydrogen evolution current density of 8 mA/cm^2 at the reversible potential, $U_{\text{RHE}} = 0$ V, corresponding to an incident photon-to-current conversion (IPCE) of 47%. Considering that only 2.6×10^{13} Mo₃S₄ clusters/cm² is present during operation, this rate of hydrogen evolution at the reversible potential corresponds to a turnover frequency (TOF) of 960 sec^{-1} for the Mo₃S₄ modified planar Si.

In order to further improve the photoelectrochemical activity of this system, we aim to orthogonalize the light capture and charge-carrier collection in the photoelectrode. To accomplish this, we prepared Si pillars with high aspect ratios using a photo-lithographic method (see Supplementary Methods). Scanning electron micrograph characterization of the pillars is shown in Fig. 2b. The resulting Si pillars are completely oriented and highly regular, with the diameter of $3 \mu\text{m}$ and the height of $50 \mu\text{m}$. The photoelectrochemical data in Fig. 2a shows that the naked Si pillars are considerably improved relative to planar Si, the limiting current density of the pillar electrode is about 16 mA/cm^2 corresponding to an IPCE of 93%, 33% higher than that of the planar Si. The photoactivity was further improved by depositing 2 nmol Mo₃S₄ cluster catalyst onto the Si pillar electrode, yielding a sample that reaches 9 mA/cm^2 at $U_{\text{RHE}} = 0$ V, the highest photoactivity measured in this study. Bubbles dislodging from the photocathode could clearly be observed under these conditions (see Supplementary Movie S1).

To confirm that the reaction taking place on the Mo₃S₄/Si pillars electrode is HER, we have run the experiment over 60 min at $U_{\text{RHE}} = 0$ V under red light irradiation with gas chromatographic (GC) product quantification (Fig. 3). During the 60 minutes the number of electrons passing through the outer circuit is 7.9 C, corresponding to 82 μmol . The evolved H₂ as measured by GC analysis of the head space is represented by red dots in Fig. 3. The measured amount of H₂ closely matches half of the number of electrons passed through the circuit (shown as the black dashed line). This demonstrates that the current is indeed due to photocatalytic hydrogen evolution with unity Faraday efficiency, and not a reduction of the Mo₃S₄ cluster. Assuming that the coverage of Mo₃S₄ clusters present on the pillar surface during operation is similar to that measured on the planar surface (the accurate working coverage on the pillared structure could not be measured by XPS), the calculated TOF of hydrogen evolution is 65 sec⁻¹ for the Mo₃S₄ modified Si pillars. Of course, the TOF is quite dependent on the light intensity. With an increase in light intensity, the photocurrent increases (see Supplementary Fig. S4), thus the TOF also increases. As shown by the blue line in Fig. 3, the current remains stable for 1 h. Furthermore, no deactivation was observed after 24 h of light/dark cycles (see Supplementary Fig. S5), provided that the concentration of O₂ is kept low (≤ 15 ppb) in the system. We note, however, that the DOE target for longevity is 1000 h of operation [30].

Comparison of the unmodified and cluster-modified electrodes in Fig. 2a shows that the limiting current under large cathodic potential suffers slightly when clusters are present. The reason for the decrease in limiting current could be hydrogen bubbles adhering to the surface causing the loss of effective surface area. The cluster-modified surface is more hydrophobic than the untreated surface making bubbles adhere much better. Fig. 2a also shows that Mo₃S₄/Si pillars have better activity than Mo₃S₄/planar Si, although the gain is modest near the onset potential. More importantly, the pillar structure increases the limiting current (and IPCE) significantly. For high-quality single-crystal Si samples at low overpotential, not much is gained by orthogonalization, except for a lower reflectance loss. However, in a cheap gas-phase grown system, where the minority carrier lifetime would be much lower, orthogonalization *i.e.* pillars would be crucial for success [20]. In effect, our pillars constitute a "model system" for VLS-grown Si pillars, and they demonstrate that solar-driven hydrogen evolution can indeed be achieved with such configurations without using any platinum-group metals.

In order to gain more insight into the nature of the active site in the Si-supported Mo₃S₄ catalysts, we performed a series of density functional theory calculations on a model system, depicted in Fig. 4. The hydrogen evolution reaction (HER), $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$, on a catalyst in contact with an electrolyte takes place

via a single intermediate state H^* (hydrogen adsorbed on the surface). Hence, the thermochemistry of the reaction can be described by a three-state free energy diagram as the one shown in Fig. 4. At standard conditions (1 bar of H_2 , pH = 0 and 298 K) the initial state, $H^+ + e^-$, is in equilibrium with the final state, $\frac{1}{2} H_2$, at $U = 0$ V versus the normal hydrogen electrode. The free energy of the intermediate state, ΔG_{H^*} , is calculated relative to hydrogen in the gas phase and is sensitive to the choice of catalyst material. Common for the highly active HER electro-catalysts, such as archetype Pt, is the prediction of a nearly thermo-neutral reaction [21], *i.e.* the calculated $\Delta G_{H^*} \approx 0$ (Fig. 4).

The criteria for an optimal co-catalyst for HER on a photocathode can be less stringent than for an optimal electro-catalyst. For a photocathode the excited electrons responsible for the reduction come at a chemical potential, given by the Quasi Fermi level of the electrons at the semiconductor electrolyte interface, which is determined by the Fermi level of the holes (the potential of the electrode measured at the dark side of the electrode) plus the photovoltage generated in the absorber material. Band bending is required for driving the photogenerated electrons to the surface and this requirement puts an upper limit on the potential (the so-called flat-band potential) of the photocathode for it to work. The flat-band potential for the *p*-Si cathode measured in our particular system is $U_{RHE} = 0.2$ V (see Supplementary Fig. S6) *i.e.* charge separation will only happen at $U_{RHE} < 0.2$ V. Based on a recent paper by Boettcher *et al.* [20], we can estimate the photovoltage approximately to be -0.55 V for the planar *p*-Si. As shown in Fig. 4, this means that at $U_{RHE} < 0.2$ V, the free energy of $H^+ + e^-$ will always be higher than ~ 0.35 eV in our particular system, indicating that catalysts with ΔG_H in the interval 0.35 – 0 eV should be good co-catalysts.

The inset in Fig. 4 illustrates the structure adopted by a ligand-free Mo_3S_4 model cluster adsorbed on H-Si(100). To neglect ligands is a justifiable approximation as test calculations show that ligands have a small effect on the calculated ΔG_{H^*} . Hydrogen preferentially binds to one of the under-coordinated sulfur atoms on the anchored Mo_3S_4 cluster. However, the hydrogen adsorption is weak, similar to the adsorption on a close-packed gold surface [21]. Thus the Mo_3S_4 clusters should not show high activity for electrochemical hydrogen evolution until the overpotential of the electrons is ~ 0.4 V, which is confirmed by experiments on Mo_3S_4/n -Si in darkness (see Supplementary Fig. S7) and it also agrees with the potential required for HER onset on Mo_3S_4/p -Si under illumination, where the reaction starts at $U_{RHE} = 0.15$ V, which corresponds to ~ 0.4 V of overpotential when the photovoltage is added. This is all shown in Fig. 4, which also illustrates why the Mo_3S_4 cluster is comparable to Pt as HER co-catalyst on the *p*-Si photocathode [6].

In summary, we show the feasibility of functionalizing a solid-state semiconductor surface with a molecular catalyst to drive solar hydrogen production. We demonstrate such a system using silicon treated with Mo₃S₄ clusters, although it should be stressed that this only addresses “half” of the water-splitting problem, namely the photocathode for hydrogen evolution. The photocathode we present contains no noble metals, yet still works with high photon-to-hydrogen efficiency in red and infrared light even with no external bias relative to the reversible HER potential. The obtained current density at the reversible potential is sufficient for use in a 10% solar-to-hydrogen efficiency two-photon “chemical solar cell”.

Methods

Electrode preparation Single crystal B-doped (*p*-type) Silicon wafers (100 mm diameter, (100) oriented, 0.5 mm thick, 2.2 Ω cm resistivity), were obtained from Okmetic. The wafers were cut into smaller 16×20 mm² Si chips. The chips were cleaned by immersion in piranha acid (3:1 v/v concentrated H₂SO₄/30% H₂O₂) and rinsed with pure water (>18.2 MΩ cm). On the back side of the Si chip, an Ohmic contact was established by embedding a coiled Cu wire in a eutectic gallium-indium alloy (Aldrich) which wetted the silicon. The Cu wire and the eutectic were subsequently covered with silver paint (SPI supplies). The Cu lead was passed through glass tubing with diameter of 2 mm. The epoxy (Loctite Hysol C1) was used to insulate the entire back side of the electrode and the Cu wire from the electrolyte. The electrode was wrapped with PTFE tape and a circular hole of 5.6 mm in diameter was made in the tape to expose an area of 0.25 cm² on the front side of the Si electrode. Before use, the Si electrode was immersed in 1% HF aqueous solution for 1 min at room temperature to strip off the native silicon oxide on the surface. The thus obtained H-terminated Si electrode was either rinsed with pure water and transferred into the photoelectrochemical cell for testing or further treated with the Mo₃S₄ cluster.

Mo₃S₄ cluster deposition A solution of the Mo₃S₄ cluster in a 1:1 (vol.) mixture of dichloromethane and methanol was prepared and diluted with the same solvent mixture to a concentration of 0.1 mmol/L. Typically, cluster-modified Si electrodes were then prepared by the following procedures: 20 μL of the cluster solution was drop-cast onto a freshly prepared H-terminated Si electrode (total loading: 2 nmol cluster). After dropping the cluster solution onto the silicon, the electrode was heated to 60 °C to flash off the solvent. Immediately after deposition, the sample was transferred to the photoelectrochemical cell.

Photocurrent measurement The light source was a 1000 W Xe lamp (Newport 66924) with a water filter for filtering out the long wave part of the radiation. The light was further filtered by an "AM1.5G filter" (Newport 81094) to approximate the solar spectrum and further with a 635 nm long-pass filter (Newport FSR-RG645) to discard the photons ($h\nu > 2$ eV). The overall light intensity was controlled using neutral density filters to either approximate the solar level for the most of the measurements reported in the paper or higher intensities. The irradiance spectrum of the light incident at the electrode surface was measured with a spectroradiometer (International Light Technologies Model RPS-900R). Photocurrents of the Si electrodes (WE) were measured in a gas-tight, three-electrode cell made from Pyrex glass with an aqueous 1.0 mol/L HClO₄ solution (J T Baker) as electrolyte, a commercial Hg/HgSO₄/sat. K₂SO₄ electrode as reference and a platinum mesh as counter electrode (CE) separated by glass frits. The potential of the commercial calomel electrode was confirmed against an in-situ hydrogen electrode before the experiment. The potential of WE was controlled by a potentiostat (Biologic VSP) and was recalculated against the reversible hydrogen electrode (RHE). The electrolyte was de-aerated by bubbling with hydrogen before and during measurement. Great care was taken to avoid the contamination of the WE (and WE compartment of the cell) with Pt from the CE. A case in point, the CE compartment is bubbled with hydrogen, ensuring that the reaction on CE is HOR (Hydrogen Oxidation Reaction) instead of the OER (Oxygen Evolution Reaction), this can minimize dissolution of Pt into the CE compartment.

Hydrogen measurement An electrode of cluster-coated silicon pillars was used as working electrode. The experiment was carried out exactly like the photocurrent measurements using the same cell. The only difference is that in order to quantify the amount of generated hydrogen the WE compartment of the cell was de-aerated using argon instead of hydrogen. During measurement, hydrogen was kept bubbling in the CE compartment (to avoid OER and possible Pt dissolution), but the CE compartment was sealed after argon bubbling. The evolved H₂ was detected by Gas chromatography (Agilent 6890 with TCD detector, molecular sieve 5A column, Ar carrier gas).

The density functional calculations The DFT calculations were performed at the RPBE level within the plane-wave pseudopotential approach. A plane-wave cutoff energy of 340 eV and a density cutoff of 500 eV were used. The Si(100)/Mo₃S₄ system was modeled using periodically repeated Si slabs, 3×3 surface unit cells wide and six layers thick, separated by at least 14.8 Å vacuum in the z-direction. Further details on the DFT setup are provided in the Supplementary Information.

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Author Contributions

Hou Y.D. and Vesborg P.C.K fabricated the electrodes, carried out electrochemistry experiments and hydrogen measurements. Damsgaard C.D., Pedersen T. and Hansen O. designed Si pillars, Björketun M.E. and Rossmeisl J. did the DFT calculations. Herbst K. synthesized the Mo₃S₄ cluster, Bech L. and Setti A.M. measured XPS and analyzed the data. Abrams B.L., Dahl S., Nørskov J.K. and Chorkendorff I. conceived the project, supervised the research work, and discussed the results. All authors contributed to the paper writing.

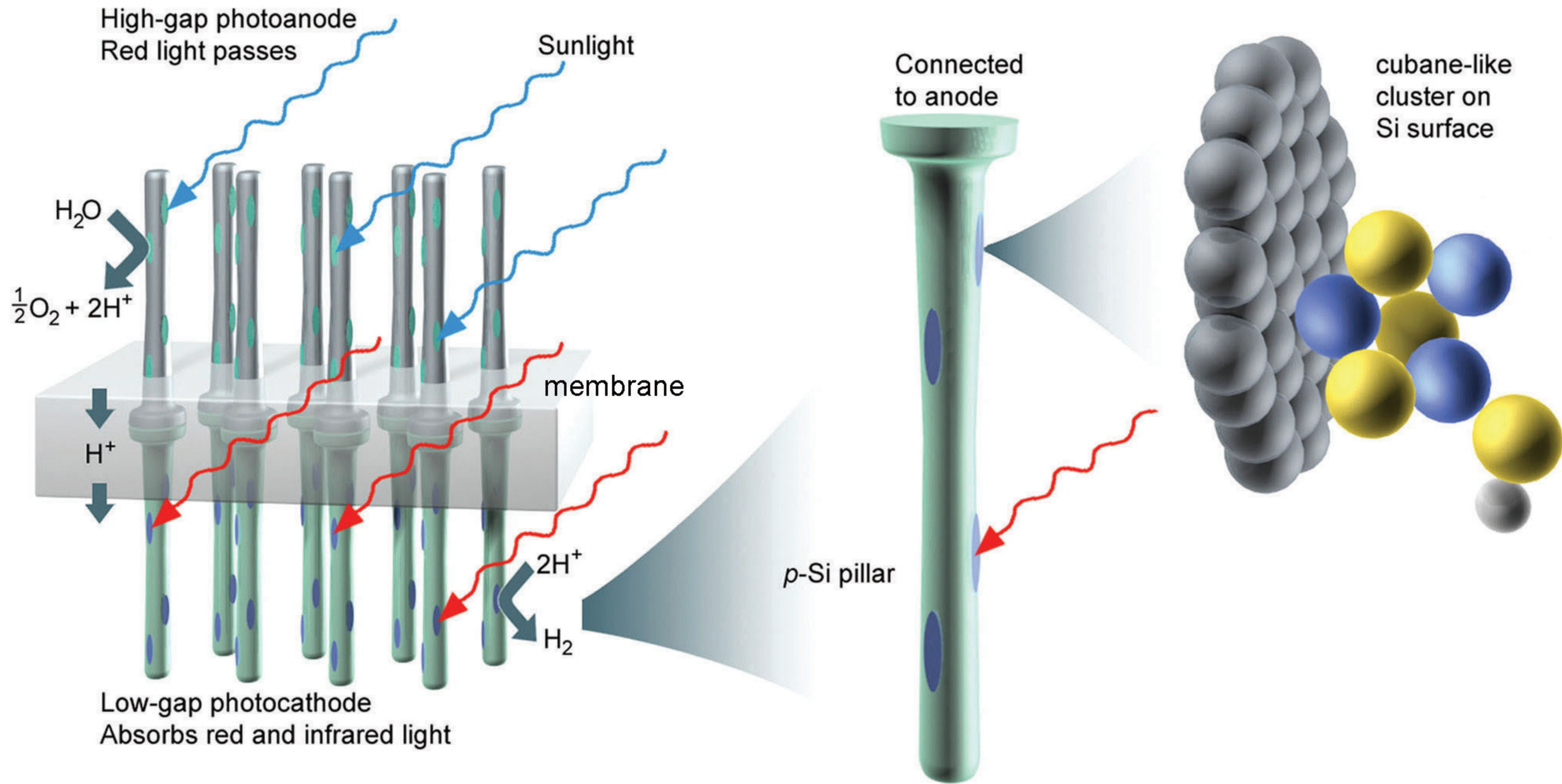
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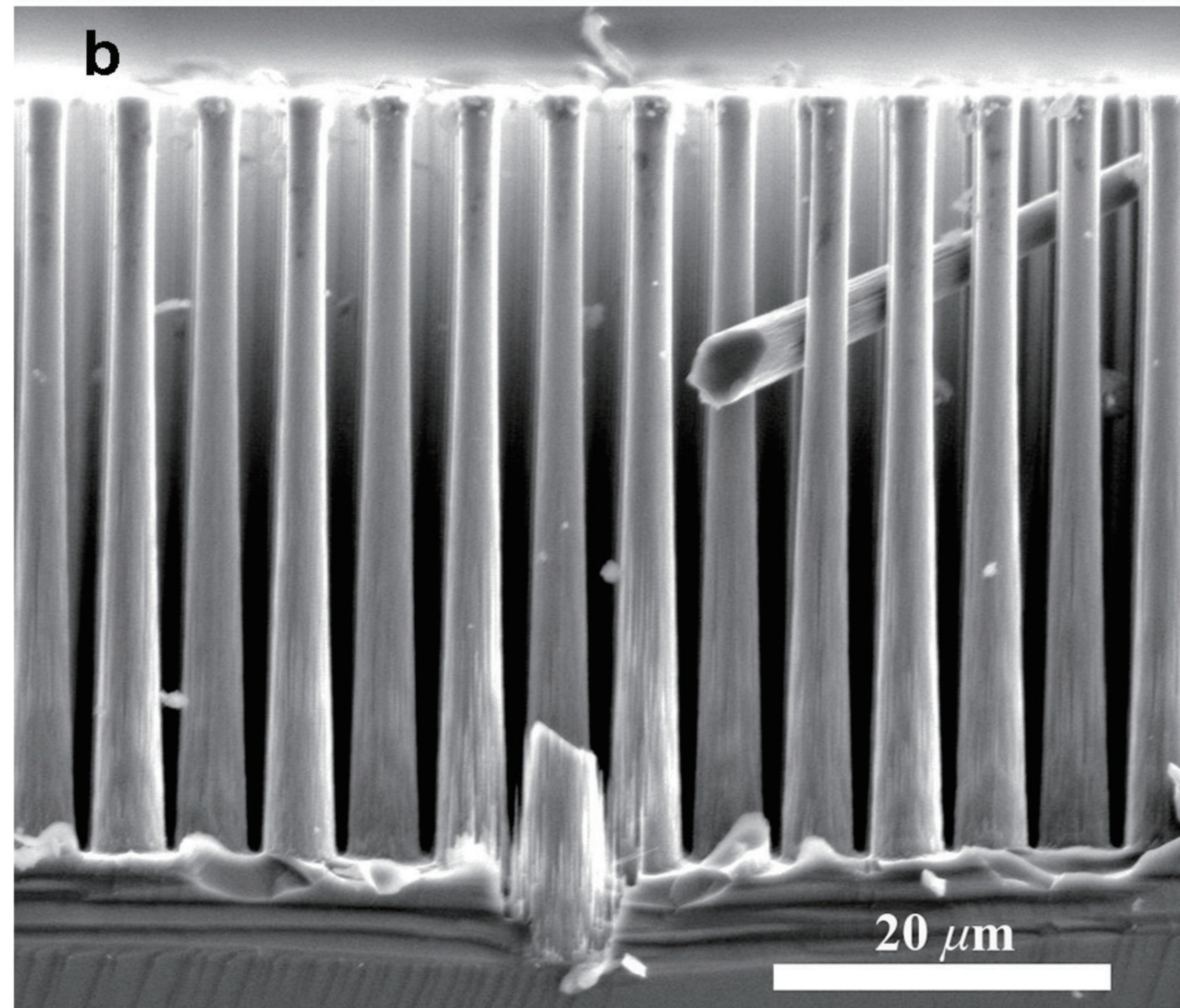
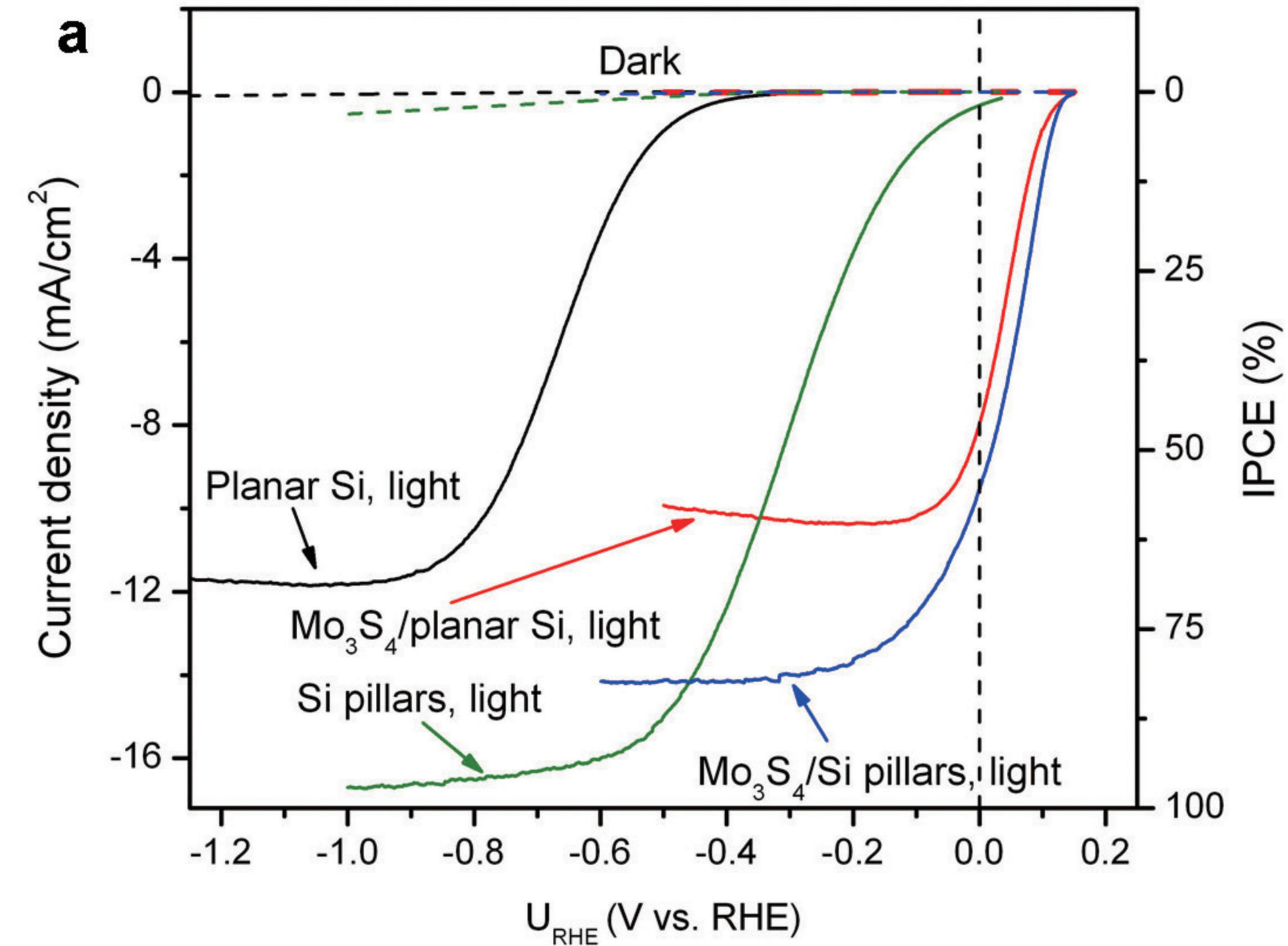
Figure 1 | Schematic of the tandem "chemical solar cell" adapted from ref [4, 19]. To the left, the entire system is shown where pillars are embedded in a proton conducting membrane. The solar light is incident from above and the blue part of the spectrum is absorbed by the anode used for oxidizing water into molecular oxygen and protons. The protons migrate through the membrane and are reduced at the cathode side by Mo_3S_4 clusters adsorbed on the Si pillars which are excited by the red part of the spectrum. As indicated in the right part of the figure, here we only deal with hydrogen evolution on the Si pillars modified with the adsorbed Mo_3S_4 clusters and excited by the red part of the solar spectrum.

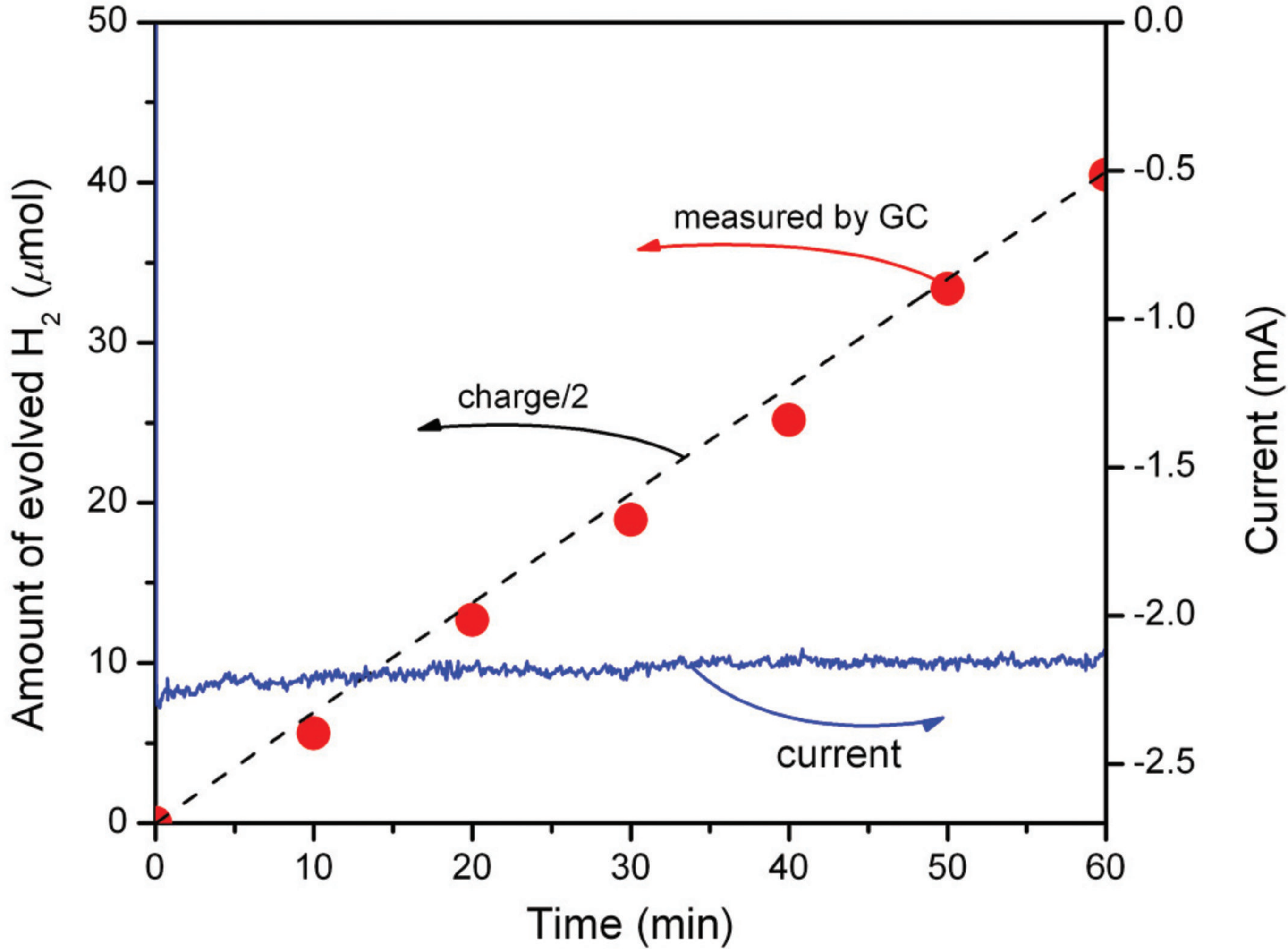
Figure 2 | The potentiodynamics runs on the photoelectrodes (a) and scanning electron micrograph of Si pillars (b). Steady-state current density-voltage (left axis) is run in aqueous 1.0 mol/L HClO_4 solution under red light irradiation ($\lambda > 620$ nm, 28.3 mW/cm²) and the calculated incident photon-to-current conversion (IPCE) is shown on the right axis. The almost horizontal dashed lines denote the current measured in darkness (almost zero mA/cm²).

Figure 3 | Stability of hydrogen evolution as a function of time measured with a gas chromatograph (left axis) and corresponding current (right axis) over $\text{Mo}_3\text{S}_4/\text{Si}$ pillars at $U_{\text{RHE}} = 0$ V. The illuminated area is ~ 0.25 cm² and the sample is under red light irradiation ($\lambda > 620$ nm, 28.3 mW/cm²). It may be seen that the current initially decays $\sim 5\%$ the first 30 min and then stabilizes. After an hour each cluster has carried out 20000 and 230000 H_2 turnovers with respect to initial (deposited) and final coverage respectively.

Figure 4 | Free energy diagrams for hydrogen evolution under three different conditions. Hydrogen evolution over a) $\text{Mo}_3\text{S}_4/n\text{-Si}(100)$ (electron conducting electrode) at $U_{\text{RHE}} = 0$ V in darkness, b) $\text{Mo}_3\text{S}_4/p\text{-Si}(100)$ at $U_{\text{RHE}} = 0$ V under illumination, and c) $\text{Mo}_3\text{S}_4/p\text{-Si}(100)$ at the flat-band potential $U_{\text{RHE}} = 0.2$ V under illumination. The free energy of adsorbed atomic hydrogen, H^* , has been obtained by calculating the free energy with respect to H_2 in the gas phase. For comparison, the free energy of hydrogen adsorbed on Pt [21] has been included.







pH=0

Free energy (eV)

0.6

0.4

0.2

0.0

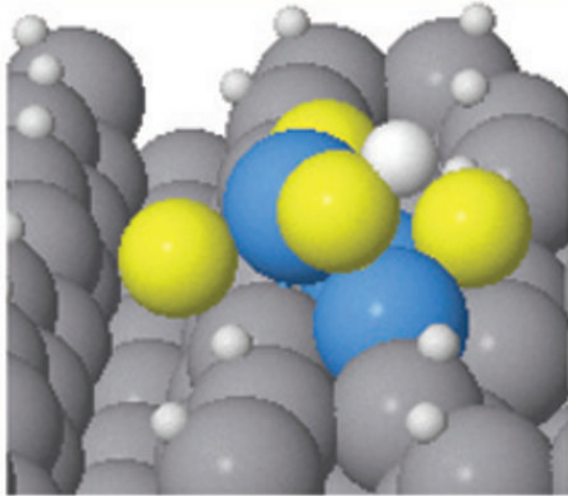
-0.2

b)

c)

a)

Mo_3S_4



Pt

$\text{H}^+ + \text{e}^-$

H^*

$1/2 \text{H}_2$

Reaction coordinate