Molybdenum sulfides—efficient and viable materials for electro- and photoelectrocatalytic hydrogen evolution

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This perspective covers the use of molybdenum dssulfide and related compounds, generally termed MoSx, as electro- or photoelectrocatalysts for the hydrogen evolution reaction (HER). State of the art solutions as well as the most illustrative results from the extensive electro- and photoelectrocatalytic literature are given. The research strategies currently employed in the field are outlined and future challenges pointed out. We suggest that the key to optimising the HER activity of MoS2 is divided into (1) increasing the catalytic activity of the active site, (2) increasing the number of active sites of the catalyst, and (3) improving the electrical contact to these sites. These postulations are substantiated by examples from the existing literature and some new results. To demonstrate the electrocatalytic properties of a highly conductive MoS2 hybrid material, we present the HER activity data for multi-wall MoS2 nanotubes on multi-wall carbon nanotubes (MWMoS2@MWCNTs). This exemplifies the typical data collected for the electrochemical HER. In addition, it demonstrates that the origin of the activity is closely related to the amount of edges in the layered MoS2. The photoelectrocatalytic HER is also discussed, based on examples from literature, with an emphasis on the use of MoSx as either (1) the co-catalyst providing the HER activity for a semiconductor, e.g. Mo3S1 on Si or (2) MoS2 as the semiconductor with an intrinsic HER activity. Finally, suggestions for future catalyst designs are given.

1 Introduction

1.1 Motivation

In the future, our energy demand will be covered by renewable resources. A significant amount of this renewable energy will be in the form of electricity from a combination of solar/wind power and biomass.1 In order to ensure continuous energy supply, the electricity has to be stored; an appealing way to solve this problem is the conversion of electricity to hydrogen.2 The water splitting reaction may be divided into the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). This perspective addresses molybdenum sulfides (MoSx) as a heterogeneous electrocatalyst and semiconducting photoelectrocatalyst for the HER. The HER is a thoroughly investigated reaction that has gained renewed attention in recent years since hydrogen plays a key role in many industrial reactions and

Broader context

Electro- and photoelectrocatalytic water splitting, powered by renewable electricity, hold promise as clean technologies for the production of hydrogen. Renewable energy coming either from sunlight or wind power is ill-correlated with consumer demand, and thus requires storing. This energy can be stored as a fuel, e.g. in the form of hydrogen. Water splitting may be carried out electrocatalytically in electrolyzers using electricity from photovoltaics or wind power. Alternatively sunlight may be converted into electron hole pairs in a semiconductor and directly used to split water, known as photoelectrocatalytic water splitting. In acidic electrolyzers and photoelectrocatalytic cells the catalyst for the hydrogen evolution reaction (HER) is a scarce archetypical platinum catalyst. Even though platinum is highly efficient, research efforts are directed towards replacing platinum catalysts with more earth abundant materials. Arguably, state of the art alkaline electrolyzers are efficient and use Ni-based catalysts, but these are limited to large-scale hydrogen production due to high capital cost. A variety of molybdenum sulfides are suitable candidates for the replacement of platinum in acidic solutions. Furthermore, molybdenum sulfides are reasonably stable, cheap, non-toxic, abundant, and active for the HER. This perspective discusses recent progress within this field and outlines future challenges.
is envisioned to be an energy carrier in the future. Hence, new efficient materials for renewable hydrogen production are greatly needed. Sustainable hydrogen, produced from electricity, may be sub-divided into two groups, depending on the electricity source, which determines the scale of hydrogen production (see section 1.1.2). (1) Electrochemical water splitting using electricity from solar cells, wind energy, and hydroelectric resources or (2) photoelectrocatalytic water splitting in which electricity is harvested directly from sunlight, as electron hole pairs in a semiconductor. This semiconductor may also be the catalyst for the HER. The common denominator in both the electro- and photoelectrocatalytic water splitting is the catalytic activity in the HER. The main difference between electro- and photoelectrocatalytic water splitting is the current density (rate) of the HER, which can differ up to three orders of magnitude. The electrocatalytic water splitting (1) is already commercialised, whereas the photoelectrocatalytic water splitting (2) is far from being efficient enough to be commercialised. It should be noted that commercial electrolysis units run in alkaline electrolytes and use Ni as the cathode material.\(^3\) Research efforts are directed towards shifting to acidic electrolytes as these units are more compact and could potentially be run in reverse to produce electricity, i.e., as a fuel cell, thus saving on capital costs.\(^4\) This approach, however, is limited by (1) the OER\(^4\) and (2) by its reliance on Pt as the cathode catalyst. Recently, a techno-economic study showed that hydrogen produced by photoelectrocatalytic water splitting could become a competitive alternative to gasoline,\(^5\) provided that a cheap and reasonably effective material for renewable hydrogen production is found.

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Assistant Prof. Søren Kegnæs received his PhD in 2009 from DTU in experimental chemistry and catalysis under the supervision of Prof. Claus Christensen and Prof. Rasmus Fehrmann, followed by work as a post-doctoral fellow. In 2011 he was employed at the Department of Chemistry, DTU, within the field of inorganic chemistry. His current research interests are associated with design and synthesis of nanomaterials, which can be applied in catalysis. His focus is on development of heterogeneous catalysts for application within sustainable chemistry.

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Professor Ib Chorkendorff got his PhD in 1985 in experimental surface science from Odense University, Denmark. After working as a post-doc with Prof. John T. Yates Jr. at Pittsburgh University, USA, he was employed in 1987 at DTU to establish the Center For Individual Nanoparticle Functionality (CINF), an experimental activity within surface physics, investigating fundamental aspects of catalysis. These activities have been broadened to include technologies for producing solar fuels utilising electro- and photocatalysis, through the common denominator of capitalising on fundamental insight for finding new and smart materials for improving energy production and ensuring a better environmental protection.
efficient system is discovered. Under these assumptions, a lower bound price of $1.60 (€1.11) per kg of hydrogen, which is the energy equivalent of one gallon of gasoline, was found to be realistic.

1.1.1 The electrocatalytic HER. Water splitting either by an (1) electrocatalytic or (2) photoelectrocatalytic route requires the HER to occur readily; hence a few general points should be made. The reaction mechanism towards hydrogen evolution will be addressed in detail later, but it is intuitive that, under acidic conditions, it involves atoms of hydrogen bound to the catalyst surface. Plotting the activity of the catalyst materials against the corresponding hydrogen bonding free energy obtained from DFT, results in a familiar volcano shaped curve attributed to the Sabatier principle.

Fig. 1 shows the volcano curve reported in literature\(^6\) for the most common catalyst materials. This illustrates why Pt is the catalyst of choice for the HER in acidic solutions. Marković et al.\(^5\) showed that, of the low index Pt facets, the most active facet of Pt is the Pt[110]. As Pt is a scarce metal with an earth crust abundance of only 0.005 mg kg\(^{-1}\) and an annual average cost of $56 (€39) per gram in 2010,\(^7\) any large-scale production of hydrogen should refrain from using this. Therefore, large efforts have been put into finding a stable, non-toxic, abundant, and cheap alternative.

In order to find a suitable replacement for Pt, a biomimetic study suggested the use of molybdenum sulfides (MoS\(_2\)).\(^8\) In nature, the active centre of nitrogenase enzymes contains one or more metal atoms usually bound to sulfur. Most nitrogenase enzymes contain one or more iron sulfur (Fe–S) clusters, and most of these enzymes also have a Mo atom bound to such an Fe–S cluster in the active centre. When fixing ammonia, these enzyme centres co-evolve hydrogen.\(^1\) This inspired the group of J. K. Nørskov to investigate hydrogen binding to MoS\(_2\) by DFT.\(^9\) The result showed that MoS\(_2\)'s hydrogen binding energy is located close to the top of the volcano curve in Fig. 1, which was subsequently verified by electrochemical measurements. The hydrogen binding free energy is obtained in DFT calculations by subtracting the free energy of the clean catalyst surface and a half a hydrogen molecule in the gas phase from the hydrogen bonded to the catalyst surface site. There are two reasons for taking a biomimetic approach rather than attaching the natural enzyme to the electrode, which is possible in some cases. One reason is that the stability of enzymes is typically limited, whereas a biomimetic catalyst may be designed for increased stability. The second is that enzymes are bulky whereas a catalyst cluster/nanoparticle is much smaller; the size of the catalyst on the electrode is often termed the catalyst footprint and should be as small as possible. The smaller the footprint, the more compact the electrolysers/photoelectrocatalytic units. Thus, the focus of the biomimetic study is only on the enzymatic centre since this plays a key role in the enzyme activity. In fact, a typical footprint of a small electron transfer enzyme (Azurin\(^{12}\)) is ~25 times larger than a cubic MoS\(_2\)\(^+\) unit\(^13\) representative of a hydrogen evolution centre of an enzyme. From this it may be speculated that the optimal catalyst is a molecule/atomic cluster. Generally, there are two ways to improve an electrocatalyst: (1) increasing the intrinsic activity of the active site by the choice of the compound; (2) increasing the density of active sites, which will also decrease the catalyst footprint. One example of the latter is the incomplete cubane, [(H\(_2\)O)\(_6\)Mo\(_3\)S\(_4\)]Cl\(_4\), which consists of Mo and S in alternating corners of a cube with one Mo corner missing, and is one of the smallest known clusters of MoS\(_2\).\(^13,14\) These molecular units consist of nothing but surface atoms/edge sites and therefore have an optimised number of active sites—in fact, these catalysts have been tested and are highly active.\(^13,14\) This type of catalyst will be described in more detail in section 2.

1.1.2 The photoelectrocatalytic HER. The photo-electrocatalytic HER relies on the catalyst material having two properties: (1) the material should be active for the electrocatalytic HER and (2) it should absorb sunlight, giving an electron hole pair with the right potential to drive the HER reaction. These properties need not necessarily be provided by the same material. Most photoelectrocatalytic materials (semiconductors) are therefore used in combination with a co-catalyst, which is often Pt. This co-catalyst specifically catalyses the HER reaction and operates as described in section 1.1.1. Since the exact same considerations apply for these systems as for the electrochemical HER, research efforts are directed at replacing Pt for photoelectrocatalytic HER as well. The scarceness of Pt is an even larger problem in the photoelectrocatalytic HER as compared to electrolysers, as large areas need to be covered with the catalyst to sustain our energy demand. To get an idea of the scale of each approach to the HER, a photoelectrocatalytic material capable of harvesting 10% of the sunlight will produce approximately 8 mA cm\(^{-2}\) photocurrent, which is significantly lower than the 1000–10 000 mA cm\(^{-2}\) for electrolysers. The difference is due to the low flux of sunlight, and therefore to the current, compared to a centralised electricity source. Furthermore, it is even more important that the catalyst footprint is smaller for the photoelectrocatalytic HER than it is for the electrochemical HER. Since the co-catalyst may interfere with the ability of the semiconductor to absorb sunlight, this also means that the catalyst must be very well dispersed. Therefore, cubanes of MoS\(_2\) are also ideal for the photoelectrocatalytic HER because they offer a structure consisting of only surface atoms/edge sites, and thus have a very small electrode footprint. One such cubane system was recently demonstrated to be highly active for the photoelectrocatalytic HER\(^15\) (see section 3). Another way to solve the...
problem of dispersion is to use an integrated system, i.e. a system in which the semiconductor is also an active component for the electrochemical HER. As MoS$_2$ is a semiconductor with a suitable 1.7 eV band gap, it is a good candidate for such a system. This leads to a separate discussion of the electrochemical HER in general and of the semiconductor properties of MoS$_2$.

1.2 Background

1.2.1 The HER & the electrochemical evaluation basics. The mechanism of the HER is thought to go via the so-called Volmer–Heyrovsky mechanism:

$$\text{H}_2\text{O}^-(aq) + e^- + * \rightleftharpoons \text{H}^* + \text{H}_2\text{O}(1), \text{Volmer reaction (acidic) (1)}$$

$$\text{H}_2\text{O}(1) + e^- + * \rightleftharpoons \text{H}^* + \text{OH}^-(aq), \text{Volmer reaction (alkaline) (1a)}$$

$$\text{H}^* + \text{H}_2\text{O}^-(aq) + e^- \rightleftharpoons \text{H}_2(g) + \text{H}_2\text{O}(1) + *, \text{Heyrovsky reaction (acidic) (2)}$$

$$\text{H}^* + \text{H}_2\text{O}(1) + e^- \rightleftharpoons \text{H}_2(g) + \text{OH}^-(aq) + *, \text{Heyrovsky reaction (alkaline) (2a)}$$

or the Volmer-Tafel mechanism:

$$\text{H}_2\text{O}^-(aq) + e^- + * \rightleftharpoons \text{H}^* + \text{H}_2\text{O}(1), \text{Volmer reaction (acidic) (1)}$$

$$\text{H}_2\text{O}(1) + e^- + * \rightleftharpoons \text{H}^* + \text{OH}^-(aq), \text{Volmer reaction (alkaline) (1a)}$$

$$\text{H}^* + \text{H}^* \rightleftharpoons \text{H}_2(g) + 2*, \text{Tafel reaction (acidic and alkaline) (3)}$$

where $*$ indicates an empty active site and $\text{H}^*$ a hydrogen atom bound to an active site. The key parameter in both reactions is the binding of the intermediate hydrogen to the catalyst surface. This indicates that plotting the activity of the catalyst material against the hydrogen binding free energy, e.g. from DFT, would result in a volcano curve. Indeed, this is the case as seen in Fig. 1. In short, a volcano curve results from plotting the catalyst activity as a function of the catalyst reactivity, which is determined by a reaction descriptor specific such as the binding energy of a key intermediate. The optimal catalyst lies at the top of the volcano curve. This catalyst has the ideal trade-off between energy of a key intermediate. The optimal catalyst lies at the top of the volcano curve. This catalyst has the ideal trade-off between catalyst activity as a function of the catalyst reactivity, which is seen in Fig. 1. In short, a volcano curve results from plotting the activity of the catalyst versus potential has an exponential behaviour, which may be simplified to eqn (4) the so-called Tafel equation (here shown for cathodic currents):

$$j = j_0 e^{-\frac{\eta}{b}} \text{ so } \ln(-j) = \ln(j_0) - (1/b)\eta \quad (4)$$

where $j$ is the current density, $j_0$ is the exchange current density, $b$ is the Tafel slope, and $\eta$ is the overpotential (the potential increases beyond the reversible potential of the half-cell reaction). This simplification only applies for cathodic currents and in the limit where $\eta$ is large, but still small enough that the current is not yet diffusion limited. The exact range is very system dependent, but often lies in the range $\eta = 0.1–0.5 \text{ V vs RHE}$ (the reversible hydrogen electrode) for the HER. As the optimal catalyst is the material that gives the highest currents at the least overpotential, it may be seen from the Tafel equation that this catalyst has a low Tafel slope ($b$) and a large exchange current density $j_0$. The exchange current density is explained in detail elsewhere, but may be viewed in this context as a measure of the electron transfer rate of a catalyst and it varies over several orders of magnitude, as seen in Fig. 1. The importance of the Tafel slope is easily recognised when one recalls the different orders of magnitude of the HER currents that both the electrochemical and photoelectrochemical hydrogen evolution require. If the Tafel slope is too high, the catalyst requires significant overpotentials to produce the necessary currents. The Tafel slope depends, in a complex way, on several factors, including the reaction pathway and the adsorption conditions of the active site. It should be noted that the Tafel slope may vary significantly for different preparations of the same material. In the case of MoS$_2$, the factors influencing the Tafel slope are not known, making it difficult to interpret differences. The interpretation of Tafel slopes, in terms of the reaction mechanism, is beyond the scope of this perspective (see ref. 20 and 21). In this perspective, we will evaluate catalysts based on the onset potential, that is, the potential at which the HER activity begins and qualitatively in terms of high, low, or intermediate Tafel slopes (see Fig. 5).

1.2.2 MoS$_2$ properties. Bulk MoS$_2$, which naturally occurs as molybdenite, has a layered hexagonally packed structure consisting of S–Mo–S sheets held together in stacks by van der Waals interactions. This material is a semiconductor with a direct band gap of ~1.7 eV. As MoS$_2$ is also active for the electrocatalytic HER, it is a potential candidate for a HER photoelectrocatalyst. MoS$_2$ is perhaps most well known as the active part of the heterogeneous catalysts for hydro-desulfurisation (HDS). The synthesis of MoS$_2$ materials has been reviewed elsewhere, and more recently in a perspective in this journal. The work on electrochemical hydrogen evolution on natural crystals of MoS$_2$ was pioneered in the 1970s by Tributsch and co-workers. DFT studies showed that the edges of a S–Mo–S sheet are the active sites, in particular the [1010] Mo-edges should have the most advantageous hydrogen binding energy of the edges considered. The verification that the edges are responsible for the activity was demonstrated in our group by using a combination of STM, and electrochemical measurements. In this study, single sheets of MoS$_2$ were grown on Au[111] by deposition of Mo in a H$_2$S atmosphere followed by annealing in H$_2$S as described by Helveg et al. This results in nanoplatelets with a truncated triangular shape exposing Mo-edges and [1110] sulfur edges, see Fig. 2. The edges of the nanoplatelets are observed as bright rims in the STM images in Fig. 2; the bright rims are suggestive of conductivity at the edge, an effect verified by DFT calculations. The total edge length was determined by STM, and was subsequently shown to correlate well with the measured electrochemical HER activity as opposed to the total area of the nanoplatelets. It is important to note that perhaps the most important inherent problem of using
MoS₂ in any kind of electrochemical reaction is the extremely low conductivity between two adjacent van der Waals bonded S–Mo–S sheets. Resistivity has been measured to be 2200 times larger through the basal planes as compared to the $10^{-1}$ to $1 \ (\Omega \ cm)^{-1}$ parallel to the planes. This means that the single layer nanoplatelets are an optimal structure compared to a multi-layer nanoparticle because electrons only need to be transferred from the support to the platelets. In a nanoparticle, as the one illustrated in Fig. 3, the electrons have to be transferred from the support to the bottom layer and then further through four platelet interfaces to reach all the edges. This increases the resistance for each traversed layer. The conductivity of the edges could suggest that charges may be passed along the edge from the substrate to the active sites as a low resistance connection, though it has not been determined whether or not this is the case. These considerations lead to the idea that stacking MoS₂ nanoplatelets perpendicular to the conductive surface may prove to be an advantageous catalyst design. This strategy is currently being pursued in our laboratory (see further in section 4).

2 The electrochemical HER

To put the HER activity of MoS₂ nanoplatelets on Au[111] into perspective it should be compared to the initial work of Tributsch and co-workers. MoS₂ on Au[111] showed an onset at $\sim 0.15 \ V$ vs. RHE, and a Tafel slope of $55-60 \ mV \ dec^{-1}$, the activity measured by Tributsch is estimated to have an onset potential of around $-0.09 \ V$ vs. RHE† with a Tafel slope of $\sim 692 \ mV \ dec^{-1}$. This Tafel slope is very high and is likely due to a large internal resistance in the bulk semiconductor. It is however, evident that the MoS₂ on Au[111] is a significant improvement to the bulk MoS₂. A subsequent study showed that MoS₂ on porous carbon paper has similar properties to the gold supported nanoplatelets, with an onset at $\sim 0.2 \ V$ vs. RHE and a Tafel slope of 120 mV dec$^{-1}$. This Tafel slope is significantly larger than that of the nanoplatelets on the Au single crystal, which was attributed to diffusion limitations through the fibrous carbon electrode. The corresponding value for the single crystal Pt[111] surface is an onset at 0 V vs. RHE and a Tafel slope of 28 mV dec$^{-1}$. The Pt overpotential is still significantly better than the one for MoS₂ as would be expected from the volcano curve, see Fig. 1.

† All potentials in this perspective are referred to the RHE (reversible hydrogen electrode) reference electrode. For details see supplementary material.

As stated earlier, there are two general strategies to improve MoS₂ electrocatalysts. The first is to improve the intrinsic reactivity of the catalyst, i.e. optimising the binding energy of hydrogen. This has previously been done by doping the MoS₂ nanoplatelets with Co. In that study, which combines DFT and electrochemical measurements on doped MoS₂ on carbon electrodes, it was found that the activity of MoS₂ is significantly increased by doping with cobalt. DFT calculations show that the incorporation of Co into the S-edges decreases the binding energy of hydrogen from 0.18 to 0.10 eV, which is close to the 0.08 eV for the Mo-edge. As a result of doping with Co, all the edges become active for the HER. In this connection, it should be noted at this point that as only 25% of the edge atoms are hydrogen covered during operation, according to the DFT calculation of the hydrogen binding free energy, hence only a fraction of the MoS₂ entities are active for the HER reaction. The hydrogen coverage is determined by the binding free energy, as increasing the coverage beyond 25% increases the interaction between two neighbouring H* species, which in turn decreases the binding free energy for subsequent hydrogen atoms (moving to the right on the volcano curve, Fig. 1). The second approach to improving the electrocatalytic activity of MoS₂ is to increase the amount of edges per mole MoS₂. Two examples of the effect of increasing the amount of edges were recently published. In the one by Li et al. MoS₂ nanocrystals were deposited on graphene by a hydrothermal reduction, using hydrazine, of both ammonium tetrathiomolybdate ($\text{(NH}_4)_2\text{MoS}_4$), and the oxidised graphene. The composite is a material with an abundance of small MoS₂ crystals dispersed on the conductive graphene. This optimises the amount of edges as the particles are very small and the conductivity of graphene ensures an efficient contact to the particles. This allows for a high loading of MoS₂ per unit area, essentially resulting in a smaller electrode footprint. They obtained an onset of approximately $-0.15 \ V$ vs. RHE and an impressive Tafel slope of 40 mV dec$^{-1}$. Similarly, Merki et al. obtained an onset of $-0.1 \ V$ vs. RHE and a Tafel slope of 40 mV dec$^{-1}$ on an electrodeposited amorphous MoS₂ thin film. This catalyst is obtained by cycling a conductive FTO (fluorinated tin oxide) glass electrode or glassy carbon electrode in a ($\text{NH}_4)_2\text{MoS}_4$ solution between two potentials. The catalyst material is not well understood at the moment, but this, together with the previous example, indicates that the enhancement of the amount of edges is the determining factor for the activity. It should be emphasised that the active compound consists of MoS₂ in valence state +4 (analogous to MoS₂) as also demonstrated by post-testing XPS analysis (note

**Fig. 2** (a) STM on MoS₂ nanoplatelets on Au [111], reproduced with permission.* (b) A molecular model of a platelet exposing both Mo and S-edges from top and side view, reproduced with permission.**

**Fig. 3** Schematic of the difference in conductivity to the active sites on nanoplatelets and nanoparticles. Modified with permission.***
that the authors refer to the material as a MoS$_2$ thin film due to the method of deposition), this is analogous to the co-catalyst studied by Tang et al.\textsuperscript{33} on CdSe/CdS nanowires. These studies show that the optimal MoS$_2$ electrocatalyst combines an efficient electrical contact with many edges sites. It would be beneficial to find a method for estimating the amount of edge sites in a sample. In the study of MoS$_2$ on carbon electrodes by our group,\textsuperscript{30} the relative amount of edges in a sample of MoS$_2$ nanoplatelets was shown to be approximately proportional to the current from an oxidation feature. By slowly scanning the potential to 0.98 V vs. RHE a shoulder at 0.70 V on the main oxidation peak corresponds to the oxidation of the reactive edges. This oxidation almost completely eliminated the HER activity, showing that MoS$_2$ is indeed being oxidised.\textsuperscript{30} A coulometric analysis of the double oxidation feature shows that the shoulder (at 0.70 V) relative to the main peak (at 0.90 V) corresponds to 8% of the total amount of MoS$_2$ oxidised. Assuming a triangular shape and size based on literature values, the 8% is attributed to the oxidation of the 25 nm of edge length per nanoplatelet.\textsuperscript{30} Another result derived in this experiment is that the number of electrons drawn to oxidise one Mo is 8.9, which is in between the 2 electrons required for the partial oxidation of MoS$_2$ to MoO$_3$ and 18 electrons required for the full oxidation to MoO$_3$ and 2SO$_2^-$.\textsuperscript{30} This result is close to the lower bound observed by Tributsch of 10 to 25 electrons per Mo atom, which was determined on natural n-type crystals.\textsuperscript{37} They attribute the divergence to either (i) the loss of non-oxidised MoS$_2$ peeling off the surface as oxygen is co-evolved, (ii) the oxidation of partially oxidised MoS$_2$ by oxygen from the solution, or (iii) the co-evolved oxygen. Regardless of the origin of the discrepancy, the method allows for the determination of the number of edges to basal plane ratio of the catalyst material and therefore the amount of active sites.

The general principle governing the amount of edges is a function of how the relative surface energy of the edges compares to the basal plane. The surface energy of the MoS$_2$ edges is reported to be 100 times larger than the basal plane surface energy (250 mJ m$^{-2}$).\textsuperscript{34} In order to increase the amount of edges, the edge surface energy should be lowered compared to the basal plane surface energy. A recent study show that if MoS$_2$ is synthesised in an ionic liquid, the resulting material is a porous structure comprising of randomly packed, and almost exclusively single sheets of MoS$_2$.\textsuperscript{35} The ionic liquid is chosen so as to match the surface tension of the MoS$_2$ edges. The synthesised MoS$_2$ materials show great promise as highly active HER catalysts and are an excellent example of a promising approach to increase the number of edges on the catalyst.

As an example of the aforementioned strategy of increasing the conductivity to a large number of edges, we present here a new strategy for producing an electrocatalyst with improved contact properties. We investigate the HER activity of multi-walled MoS$_2$ nanotubes (MWMoS$_2$) coated onto multi-walled carbon nanotubes (MWCNT), making core/shell composite nanotubes, MWMoS$_2$@MWCNT. To our knowledge, this is the first time this composite structure has been investigated for its HER activity. The core/shell construction is expected to have excellent properties due to the high surface area of conductive MWCNTs as well as the catalytic activity of MoS$_2$. Furthermore, we demonstrate that the activity of this composite electro-catalyst is governed by the edge sites of the MoS$_2$ just as was the case for nanoplatelets of MoS$_2$.\textsuperscript{4} Following the synthesis procedure described elsewhere (and in the ESI),\textsuperscript{†} MWMoS$_2$@MWCNT was prepared and characterised using HRTEM (see Fig. 4). The HRTEM images show that the pristine material (see Fig. 4(a)) has a coating of MoS$_2$ with most of the MoS$_2$ sheets (seen as dark lines with white edges due to the Z contrast) aligned randomly to one another resulting in exposure of several edges as accessible active sites whereas the MoS$_2$ coating of the annealed sample (see Fig. 4(b)) has most of the MoS$_2$ sheets aligned parallel and a more even wall thickness, which indicates fewer active sites per tube. Following the procedure given in the ESI,\textsuperscript{†} carbon paper electrodes were made with an approximate loading of 75 µg MWMoS$_2$@MWCNT. By using SEM-EDS measurements, the amount of MoS$_2$ was determined to be approximately 215 nmol per electrode (the average MoS$_2$ loading was determined to be 46 wt% in the MWMoS$_2$@MWCNT).

The activity of the pristine MWMoS$_2$@MWCNT sample is shown in Fig. 5. The onset potential for the electrochemical HER is around −0.15 to −0.20 V vs. RHE, which is what has previously been observed for MoS$_2$.\textsuperscript{30–32} The Tafel slope is measured to be ≈109 mV dec$^{-1}$ (exchange current density, $j_0$ = ~4.0 × 10$^{-4}$ mA cm$^{-2}$ geometric), which is comparable to the result from MoS$_2$ on carbon electrodes.\textsuperscript{30} However, the Tafel slope in particular is much larger than that reported by Li et al.\textsuperscript{31} and Merki et al.\textsuperscript{32} This indicates that the improved conductivity through the MWCNTs alone did not reproduce the advantageous Tafel slope of Li et al.\textsuperscript{31} and Merki et al.\textsuperscript{32} or that the conduction through the inner layers of MoS$_2$ is limiting, i.e. reducing the number of layers would increase activity. As the latter could not be altered in this synthesis, this effect was disregarded. Another important factor for the activity is the number of edges per tube—if this could be increased the activity would too. To investigate this notion, the opposite experiment was carried out and the number of edges was reduced. The nanotubes were annealed in a tube furnace at 800 °C in argon for 2 and 8 h, respectively. The resulting CV curves for these materials are show in Fig. 5.

From Fig. 5, it can be seen that the onset potential shifts to more negative values, indicating a loss of activity. As the HER activity was correlated to the amount of edges the loss of activity would indicate that the nanotube composites consist of fewer edges after the annealing. From Fig. 4(b), it can be seen that after only 2 h of annealing, the tubes became smoother than the
The geometric area of the electrode was 1.5 cm². 

coincides with a significant decrease in the HER activity (below pristine sample, but decreases in the subsequent scan, which respectively). This feature is clearly seen in the first scan of the MWMoS₂@MWCNT, showing the characteristic oxidation feature further. The CV of the pristine, and the 8 h annealed the oxidation of MoS₂ and was therefore not investigated some surface groups on the tubes. It is not, however, relevant to the CV of the pure MWCNTs (Fig. 6(c)), it is ascribed to redox activity of impurities from the carbon nanotube production or the potential at a scan rate of 20 mV s⁻¹. The Tafel slope also changed to a slightly larger value after the annealing procedure. The Tafel slope increased to 139 mV dec⁻¹ (j₀ = ~3.2 × 10⁻⁴ mA cm⁻² geometrical) and 139 mV dec⁻¹ (j₀ = ~6.2 × 10⁻⁷ mA cm⁻² geometrical) for the 2 and 8 h of annealing, respectively. To further investigate the reduction in the amount of edges, the tubes were electrochemically scanned to positive potentials, where the oxidation of edge sites and basal planes is observed. The CVs of the oxidation scans for the pristine, 8 h annealed and the pure MWCNTs are shown in Fig. 6.

Fig. 5 Cyclic voltammetry investigations of the pristine, 2 h annealed, 8 h annealed MWMoS₂@MWCNTs composite and pure MWCNTs. (a) Current density versus potential at a scan rate of 20 mV s⁻¹. (b) Tafel plot; the scan rate was 5 mV s⁻¹, the electrolyte was 0.1 M HClO₄ (pH 1.24), and the geometric area of the electrode was 1.5 cm².

pristine tubes (Fig. 4(a)). This supports our conclusion that the decrease in activity is correlated with the abundance of edge sites. The Tafel slope also changed to a slightly larger value after the annealing procedure. The Tafel slope increased to 139 mV dec⁻¹ (j₀ = ~3.2 × 10⁻⁴ mA cm⁻² geometrical) and 139 mV dec⁻¹ (j₀ = ~6.2 × 10⁻⁷ mA cm⁻² geometrical) for the 2 and 8 h of annealing, respectively. To further investigate the reduction in the amount of edges, the tubes were electrochemically scanned to positive potentials, where the oxidation of edge sites and basal planes is observed. The CVs of the oxidation scans for the pristine, 8 h annealed and the pure MWCNTs are shown in Fig. 6.

Fig. 6(a), (b), and (c) for the three materials, show a dominant oxidation peak near 0.3 V and a broad reduction shoulder below 0.2 V vs. RHE. Since these features are the only ones present in the CV of the pure MWCNTs (Fig. 6(c)), it is ascribed to redox activity of impurities from the carbon nanotube production or some surface groups on the tubes. It is not, however, relevant to the oxidation of MoS₂ and was therefore not investigated further. The CV of the pristine, and the 8 h annealed MWMoS₂@MWCNT, show the characteristic oxidation feature of MoS₂ at more than 1.0 V vs. RHE (Fig. 6(a)(II) and (b)(II), respectively). This feature is clearly seen in the first scan of the pristine sample, but decreases in the subsequent scan, which coincides with a significant decrease in the HER activity (below ~0.2 V, see Fig. 6(a)(I) and (b)(I)). This indicates that the MoS₂ edges and basal planes are being oxidised and removed, and is therefore not seen for the MWCNTs sample (Fig. 6(c)(II)). Apart from a shoulder at 0.7 V, which was not observed, this behaviour of MoS₂ is similar to the behaviour observed in literature. The absence of this shoulder characteristic of the edge oxidation agrees well with the previous statement that the hybrid material contains relatively few edges as compared to a nanoplatelet. The oxidation feature of the basal planes was very small for the annealed samples, which is likely due to the well aligned and large S–Mo–S sheets after annealing as oxidation is thought to propagate from the edges. When the annealed samples were electrolytically scanned the second and third time to the oxidising potentials, the HER activity surprisingly increased. We speculate that this increase in activity is likely due to either the etching into pyramidal structures (see Fig. 7(b)) or the etching from starting at the edges and in pits on the basal planes, which may then propagate into wide edges (see Fig. 7(b)). A pyramidal etching pattern was previously observed by Tenne and Wold on n-type WSe₂ bulk crystals, indicating that this type of etching could have occurred on the MWMoS₂@MWCNT samples.

It has been demonstrated that the HER active edges may be annealed away for systems containing defect sites on multi-sheet MoS₂ as seen in TEM. Some of the lost HER activity may be recovered by scanning the potential to oxidising values several times. It was also shown that for the pristine sample with an abundance of active edges, the activity is reduced significantly upon scanning to oxidising potentials. The hybrid system investigated here would have greater potential if the numbers of edges per mole MoS₂ could be increased further, mainly due to the large active surface area of the MWMoS₂@MWCNTs hybrid material. It is the authors’ opinion that is the oxidation of MoS₂ sheets could be directed towards pitting rather than the edges, this would provide a potential route for increasing MoS₂’s HER activity post-synthesis, a so called top-down synthesis route; this is part of the on-going work in our group.

As stated in the introduction, the smallest molecular unit of MoS₂ is the cubane structure, which consists of only surface atoms/edges. The cubane has a very small electrode footprint; it is an excellent example of the strategy of increasing the number of active sites to improve the catalytic activity. This structure (and the approach taken to investigate it) is also a good example of a bio-mimetic approach to catalyst design. The central motif of the nitrogenase enzyme is an [Fe₄S₄] motif connected to a Mo atom. The iron-sulfur cluster is an example of a cubane structure consisting of a cube with metals and sulfur or oxygen in alternating corners. The iron–sulfur cluster is not stable in air, so instead [Mo₃S₄]” incomplete cubanes were considered by our group. These clusters contained a coordination shell of water molecules and chlorine counter ions, resulting in a hydrophilic molecular catalyst, [(H₂O)₆Mo₃S₄]Cl₄. These clusters were loaded onto HOPG (highly oriented pyrolytic graphite) electrodes and characterised by in situ STM and electrochemistry. At a loading of 0.016 nano-mole clusters, which is three orders of magnitude less than that investigated for MoS₂ on carbon electrodes, an onset potential of ~ −0.2 V vs. RHE and a Tafel slope of ~120 mV dec⁻¹ was observed. The high Tafel slope could be due to diffusion limitations on the planar substrate in a similar manner as was observed for MoS₂ on carbon electrodes. Unfortunately, the hydrophilicity of the cubane structures made the activity decrease over time due to desorption of the catalyst. These cubanes were also investigated.

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on Au[111] and the same general trends were observed irrespective of substrate. Finding a way to anchor molecular structures such as cubanes, to a surface is a challenge that needs an increased understanding in order to fully exploit the potential of such structures. One possibility for achieving this is to change the ligand to obtain a lower cluster hydrophilicity, which would potentially increase the cluster adhesion. The oxidation states of individual atoms in the incomplete cubane structure during the HER is of great interest because by stabilising this state, the HER activity could potentially occur at a more positive bias. It has been determined that the reduction of the third Mo atom from the Mo$^{4+}$ to Mo$^{3+}$ accompanies the HER. This means that the cubane structures’ HER activity could potentially be improved by changing the ligands or completing the cubane cluster with a heteroatom to stabilise this valence state. This has not been done or verified experimentally, but it is an example of the importance of studying the oxidation states for both the complete and incomplete cubanes to gather further fundamental knowledge of these systems and potentially gain ideas on how to improve activity.

Another requirement for a catalyst, which should attempt to compete with Pt, is that it should be able to be produced on an industrial scale, which is unlikely to be feasible for the cubanes. That being said, the approach to select the cubane motif as a catalyst candidate is a good example of the bio-mimetic approach to catalyst design and a potential strategy for the optimisation of the number of active sites on MoS$_x$ electrocatalysts. Recently, in another bio-mimetic study, H$_2$ evolution was catalysed by MoS$_2$ on a liquid water/oil interface (to simulate a cell membrane). When this system was chemically or electrochemically biased by lyophilic electron donors the HER activity was observed. This demonstrates the versatility of MoS$_2$ in catalysing the HER.

In summary, MoS$_x$ nanomaterials offer a suitable alternative to the expensive and scarce Pt as an electrochemical HER catalyst. The primary concerns for the use of MoS$_x$ are as follows: (1) optimise the amount of edges per area of electrode. This has been done in several ways in literature either by coating MoS$_2$ nanocrystals onto graphene or depositing amorphous thin films, or using molecular catalysts, such as the cubane structure consisting of nothing but edge atoms, or alternatively Co-doping the S-edges to be as active as the Mo-edges, so that all edges are equally active. (2) Optimise the conductivity and diffusion properties to and from the MoS$_x$ units. In this work, we presented the MWMoS$_2$@MWCNTs composites, as an example of this. The optimal effect of this strategy is also exemplified by the MoS$_2$ nanocrystals on graphene. (3) Improve the inherent MoS$_2$ activity by increasing the hydrogen binding free energy slightly. This has not been done so far, but potential strategies include doping and substrate effects. The authors believe that the recent progress in optimising the number of edges in bulk MoS$_x$ materials demonstrates how much potential strategy (1)
The direct utilisation of sunlight to create the driving potential needed for producing hydrogen by water splitting is appealing because it, in principle, allows for much simpler and potentially more efficient systems rather than the combination of solar cells and electrolysis units. When discussing the use of sunlight, it is prudent to recall the energy, and intensity of the incoming photons on the earth’s surface, i.e. the solar spectrum in terms of the number of incident photons as a function of energy. In Fig. 8, such a solar spectrum at standardised conditions (AM 1.5) is shown.\cite{40}

Based on this, one may calculate the available current density that can be produced by any given semiconductor absorbing all solar photons with energies above the semiconductor band gap. Using these calculations, as well as the driving force required for water splitting, it is possible to estimate the upper limit of solar energy to hydrogen conversion efficiency (STH). The driving force needed for water splitting is 1.23 eV. This is the thermodynamic limit, however, any OER catalyst needs a substantial overpotential for oxygen evolution. Although there are catalysts that can operate as low as 0.2 V,\cite{41} they are based on scarce metals such as Ru and Ir oxides, which are not a viable solution. Therefore, more abundant materials must be chosen for this reaction as well. Potential candidates are nanostructured cobalt and manganese oxides, which show promising low overpotentials (around 0.4 V) for the OER; however, these have not yet been realised for the type of systems discussed here.\cite{42,43} The HER is not as demanding and an overpotential of 0.1 V is within reach using catalysts made with abundant elements. Thus, 1.7 eV is the minimal driving force needed for water splitting. Here, driving force means the chemical potential of the electron-hole pairs generated in the semiconductor under solar light illumination, also known as the photo voltage in a photovoltaic cell. When the semiconductor is operated close to maximum power, the driving force is reduced by approximately 0.5 eV as compared to the band gap, leading to an additional increment in the required band gap for the semiconductor to do water splitting.\cite{44,45} Under these assumptions, a single band gap of $E_{\text{G1}} = 2.2$ V is needed to run the water splitting at a reasonable rate. The amount of photons that can be absorbed by such a semiconductor can be found by integrating the solar spectrum from the highest energy photons in the UV down to 2.2 eV. This gives an upper STH limit of 13%. It is obvious that a large portion of the solar spectrum is not used. However, if two semiconductors with different band gaps absorb different parts of the solar spectrum they can be combined to generate the required driving force; resulting in a higher efficiency. This approach is referred to as the tandem approach.\cite{46,47} The ideal tandem design would consist of two semiconductors, appropriately matched and connected so that the blue part of the spectrum from high energy photons down to $E_{\text{G1}}$ would be harvested by a semiconductor with a large band gap. The red part would be allowed to pass through the large band gap semiconductor and would be harvested by...
a semiconductor with a smaller band gap, $E_{G2}$. The second semiconductor would then absorb photons with energy between $E_{G2}$ and $E_{G1}$. This idealised design is illustrated in Fig. 10. The sum of the two band gaps required would thus be 2.7 eV (the difference between the driving force and the band gap is 0.5 eV for each semiconductor) and the two band gaps must be matched so that the number of photons captured by each of them are equal, i.e., $\int_{E_{G1}}^{E_{G2}} F(\varepsilon) d\varepsilon = \int_{E_{G1}}^{E_{G2}} F(\varepsilon) d\varepsilon$, where $F(\varepsilon)$ is the number of photons per second per m² per eV in the solar spectrum. The efficiency can now be optimised by varying the two band gaps under the constraint: $E_{G1} + E_{G2} = 2.7$ eV. The STH efficiency may then be plotted against $E_{G1}$ as shown in the insert of Fig. 8.

It is apparent that the tandem design, for its ability to harvest nearly 28% (at $E_{G1} \sim 1.7$ eV, and $E_{G2} \sim 1.0$ eV) of the solar light, prevails over the single semiconductor for which a band gap of $E_{G1} = 2.0$ eV is needed. This is due to the larger amount of the solar photons that can be absorbed by the small band gap semiconductors. Naturally, this gain in efficiency comes with the complexity of having to use two semiconductors. On the other hand, this also allows for higher degrees in freedom of materials choice and corrosion protection. The 1.7 eV for the large band gap semiconductor in the tandem approach corresponds to materials such as CdSe, which could then be matched nicely with a low band semiconductor, such as Si (band gap = 1.13 eV). Unfortunately, neither of these materials is stable as a photoanode catalysing the OER. However, Chen et al. recently demonstrated that a thin TiO₂ layer deposited on n-type Si protected the Si producing a stable photoanode. In this system matched so that the number of photons captured by each of them.

The sum of the two band gaps required would thus be 2.7 eV, indirect band gap at around 1.2 eV, and the band position slightly more positive than that for the HER. This makes MoS₂ a promising candidate for use in a tandem approach for the HER side if the conduction band could be pushed to slightly more negative values (see Fig. 9(a)). This means that MoS₂ will not evolve hydrogen when illuminated unless a negative bias (see Fig. 9(b)) or quantum confinement is introduced. These options also constitute the strategies invoked in literature to improve MoS₂ activity, along with the three strategies from section 2 to improve the electrocatalytic HER activity. Negative bias is not a viable solution for the photoelectrocatalytic HER and will not be discussed further. One example of the strategy to widen the band gap of MoS₂ by quantum confinement is the work of Wilcoxon and co-workers. Nanoparticles that were highly crystalline down to 4 nm, and also smaller less crystalline particles, were tested for photo-oxidation of the organic pollutant phenol and pentachlorobenzene and they showed reasonable activity. The increased activity is ascribed to the quantum confinement giving a larger oxidation potential (as a result of the valence band lying at a more positive value) and superior electron-hole separation. The former reason is caused by the particle size being close to the Bohr exciton radius (2 nm). This underlines the most outstanding feature of MoS₂ for photoelectrocatalysis, i.e. that it may function both as the semiconductor and the catalyst material. This leads us to define two possible applications of MoS₂ in photoelectrocatalytic water splitting: (i) the use of MoS₂ as both the semiconductor and the HER catalyst and (ii) the use of an alternative semiconductor in combination with MoS₂ as the HER catalyst. The use of MoS₂ as both the absorber and catalyst will be discussed first.

In the early studies of MoS₂ by Tributsch and co-workers, the photoelectrocatalytic activity of natural crystals of MoS₂ was investigated. They found that both n-type, p-type, and intrinsic semiconductors occur, but they did not determine the origin for any of them. As the scope of this work is the HER, we will focus on the p-type semiconductors and only note that high photo-efficiencies are obtained for n-type crystals when operated in aqueous iodine/iodide and non-aqueous solutions. Interestingly, the photocorrosion always occurs for n-type MoS₂ in aqueous solution but is almost completely suppressed by iodine or in 15 M LiCl or LiBr, which results in the photo-oxidation of chloride/bromide to chlorine/bromine with as high as 6.1% photon to product efficiency (>95% Faradaic efficiency, i.e. <5% photo-corrosion). For p-type MoS₂, the highest photocurrents observed were ~0.5 mA cm⁻² at ~0.3 V vs. RHE, by Tributsch and Bennett and ~0.32 mA cm⁻² at ~0.3 V vs. RHE, by Fujishima et al.; these remain the best that we could find in literature. Fujishima et al. also biased the p-type material to ~−0.8 V vs. RHE at which point they measured a photocurrent of 1 mA cm⁻². More recently, Chen et al. reported a double gyroid MoS₂ structure, which exhibited ~0.03 mA cm⁻² photocurrent for the HER at 0.07 V vs. RHE. The double gyroid structured thin film consists of interconnected randomly oriented pores. This type of structure illustrates the primary concern in designing efficient photoelectrodes. On one hand, the amount of material should be large enough that a significant part of the light is absorbed. On the other hand, the dimension of the structural units of the material should be small enough that the electrons/holes can reach the surface and carry out the reaction. The diffusion length of the electrons and holes is determined by multiple factors and may vary over several orders of magnitude.
Fig. 9  Band gap position for (a) MoS₂ and (c) Si, respectively at the flatband potential. In addition (a–d) show the redox levels for the HER on cubanes and the Mo-edge on MoS₂ nanoplatelets. From the figure it is seen that the HER does not occur spontaneously on bulk MoS₂ but requires additional quantum confinement, or high p-type donor concentrations. In (b) the MoS₂ is biased enough that the HER occurs, the exact potential cannot be defined. On Si the HER occur readily even at slightly positive bias with ascorbic acid as an electron donor, the HER activity of this system should be concerned with circumventing this issue.

The second way to utilise MoS₂, as a photoelectrocatalyst is to use the electrocatalytic HER activity together with a good photon absorber (exemplified for Si in Fig. 9(c)). In these systems, the distinct difference to pure MoS₂ is clearly seen, as in these systems the photon absorber may be freely chosen to provide the sufficient photon absorber, ruthenium trisbipyridine (Ru(bpy)₃). After adding ascorbic acid as an electron donor, the HER activity of this colloidal system was evaluated and yielded good hydrogen production rates. Another interesting system is the use of MoS₂ nanoparticles deposited onto CdS as a colloidal system and a photocathode. In the colloidal system, electron donors, such as lactic acid, glycerol, ethylene glycol, ethanol, or methanol, were added to avoid photocorrosion of the CdS. With this system, hydrogen production rates improved from around one-and-a-half up to two times the activity of the same amount of Pt, by weight. This demonstrates a favourable interaction between MoS₂ and CdS. It should be noted that the loaded MoS₂ are stacked plate structures, so if single-layer MoS₂ platelets could be used, the low conductivity from one S–Mo–S sheet to another could be circumvented. This line of thought inspired Frame and Osterloh to use exfoliated MoS₂ as a co-catalyst on CdSe to increase the hydrogen production from a sulfite/sulfide sacrificial agent solution. It is well known from literature that lithium intercalation followed by oxidative exfoliation results in a colloidal suspension of single sheet MoS₂. More recently, exfoliation was achieved by direct solvent extraction using ultrasonication. A colloidal suspension prepared by intercalation was then loaded onto CdSe nanoribbons resulting in up to three times improved activity as compared to a 4 nm Pt nanoparticle loaded sample. Very recently Tang et al. showed that in situ reduced MoS₂ (similar to the electrocatalyst by Merki et al.) on CdSe/CdS nanowires has a HER activity comparable to that of Pt—unfortunately this reduced MoS₂ catalyst continuously dissolves. This demonstrates that just as for the electrochemical HER, the photoelectrocatalytic HER also relies on the number of Mo-edges. Further increasing the number of edges for these systems will result in a significantly increased activity. MoS₂ on different metal oxides has also been tested for the photocatalytic oxidation of organic pollutants but this topic is beyond the scope of this perspective.

Returning to the bio-mimetic concept described in the Electrochemical section, our group recently showed that impressive...
Photocurrents could be achieved by loading hydrophobic [Mo₃S₄]⁺ onto vertically aligned pillars of p-doped Si. This is an example of the HER side of an electrode based tandem approach. A schematic drawing of how this system could be envisioned is shown in Fig. 10(a) and the electron transfer is illustrated in Fig. 9(c). These cubane structures have methyl-cyclopentadienyl ligands to avoid deactivation by dissolution of the hydrophilic cubanes. The p-doped Si wafer was tested both as a planar single crystal electrode and with a vertically aligned pillared structure. Si is an abundant element, but it is rather energy consuming to manufacture into pure single crystals as the ones used here. On the other hand, a specialised industry already exists for this in the electronics and solar cell industries. As these industries have optimised the energy consumption for the purification processes, pure Si is now a relatively cheap and facile material. The pillared structure has the same advantage as the double gyroid structure, i.e., photons scattered by the surface may be re-adsorbed while the electrons maintain a small diffusion length to the surface where they should react. The light absorption and the carrier diffusion is well understood for Si, which allows for etching Si into pillars of dimensions close to the theoretical optimum. In the case of cubanes on Si, a dimension of 3000 by 50 000 nm, which is the requirement for vapour phase deposition, pure Si is now a relatively cheap and facile material. The vaporisation processes, pure Si is now a relatively cheap and facile material.

The use of MoS₂ nanoplatelets to increase the available photoelectrocatalytic activity is demonstrated that Pt on planar Si shows this photocurrent at +0.16 V vs. RHE. Accordingly, Pt is still more efficient than the cubanes. However, this still shows that MoSₓ species materials show great promise as co-catalysts to be used in the photoelectrocatalytic H⁺ reduction, especially as these are effective and made from more abundant elements than Pt catalysts. The stability of the cubane silicon system showed good promise in the absence of oxygen, however, it deteriorated very fast in oxygen. This issue is most likely due to the oxidation of the silicon–cubane interface. The cubane–Si photocathode is a very efficient system, but if currents are to be obtained at positive bias vs. RHE, then this system is not enough. The reason for this is illustrated in Fig. 9(c), as the positive bias is applied beyond the flat band potential at approximately +0.2 V vs. RHE. Fig. 9(c) (the exact value depends on pH and doping level) beyond this point band bending inverts, electrons are repelled from the solution interface and the HER activity is stopped. More active HER catalysts than cubanes, e.g., Pt and the Mo-edge of MoS₂ (Fig. 9(c)) could potentially have a higher activity at this bias, but p-type Si cannot perform the HER at more positive potentials. The use of MoS₂ nanoplatelets to increase the available photocurrent at 0.1–0.16 V vs. RHE is part of the ongoing work in our

**Fig. 10** (a) Artistic representation of a tandem device for water splitting in which Si-pillars and cubanes are shown to preform the photoelectrocatalytic HER. (b) Photoelectrochemical measurements for [Mo₃S₄]⁺ on vertically aligned pillars of p-doped Si. Reproduced with permission.
laboratory. Recently, Lewis and co-workers showed that the limitations due to the flat band potential of Si can be overcome by introducing a heavy surface n-doping of p-type Si-nanowires grown by chemical vapour deposition (pn-junction Si-nanowires). Such a sample produced a photocurrent of $\approx 2.5$ mA cm$^{-2}$ at $\approx +0.45$ V vs. RHE, by using Pt as the HER catalyst and it is therefore very relevant to find alternative HER catalysts to Pt for such a surface. They observe the same photocurrent as for the Pt on planar p-type Si, but at 0.3 V more positive bias. The semiconductor physics behind this efficiency increase is beyond this perspective and can be perused in other literature.\(^6\) As the pn-junction system also uses Pt as the co-catalyst, it would seem obvious to load cubanes onto such nanowires, however, the improvement would be small as the overpotential of the cubanes is approximately 0.4 V.\(^{15}\) The overpotential would then counterbalance the effect of the pn-junction. This illustrates that MoS$_2$ catalysts are close to the activity of Pt at slightly negative biases, but as soon as the bias becomes positive, an even better catalyst is needed. The pn-junction Si-nanowires is one of the most promising future designs of the Si-based photocathodes. If an efficient and abundant co-catalyst can be developed, this approach could prove to be a viable solution to perform the photoelectrocatalytic HER. It is our belief that optimising the cubanes to have the same or less overpotential as the hydrophilic cubanes tested for the HER, demonstrated that using MoS$_2$ as both the absorber and catalyst is intuitive that using MoS$_2$ as both the absorber and catalyst is a good choice. However, the origin of p-type conductivity in bulk MoS$_2$ is not well understood and there are not many synthesis routes for such materials. The use of nanoclusters of highly crystalline MoS$_2$ shows good photoactivity for organic pollutant removal, but this approach has not been applied to the HER. Using a p-doped Si wafer to which cubanes were attached has been demonstrated recently to be a very efficient system realising activities close to that of the Pt analogues. We have outlined that the recent study on pn-surface junction Si wafers and nanowires provides a promising future application of MoS$_2$ to replace the Pt used as the co-catalyst for the HER in these systems. In such a system, MoS$_2$ could be used either as cubane or MoS$_2$ nanoplatelets.

Pt is the archetypical catalyst for the HER as it is exceedingly efficient. However, due to the scarcity of Pt and the resulting high price, it seems likely that if hydrogen is to become a future energy carrier or simply a renewable chemical, new catalysts must be found. We have argued that MoS$_2$ or other molybdenum sulfides such as cubane clusters are a viable and effective alternative to these ends.

Two examples of our bid on a superior catalyst design for MoS$_2$ based photocathodes are shown in Fig. 11. These two designs optimise the electrocatalytic activity by increasing the amount of edges of the MoS$_2$. Furthermore, aligning the basal planes of MoS$_2$ perpendicularly to the current collecting substrate optimises the conductivity from the active site to the supporting electrode. This allows for the metallic conductive edges to be optimally utilised. The two designs also show the general routes to make efficient MoS$_2$ photocathodes, \textit{i.e.} (1) using both the semiconducting and the electrocatalytic properties of MoS$_2$ (Fig. 11a) and (2) only using the electrocatalytic property in combination with some other semi-conducting material such as p-type Si pillars (Fig. 11b). In the first design (Fig. 11a), the catalyst consists of concentrically aligned MoS$_2$ nanotube stubs of slightly shorter length in the radial direction. These nanotubes should be stubs as they ideally should not be very long in order to minimise the amount of inactive tube wall. This allows for an optimised amount of edges while keeping the layered structure of MoS$_2$ and, hence, the photon absorbing properties intrinsic to the bulk material. This design relies on the electrons being conducted along the individual MoS$_2$ sheets.
Fig. 11  Idealised photocathode designs for potentially optimised MoS$_2$ system. (a) This shows concentrically aligned MoS$_2$ nanotube stubs of a slightly shorter length in the radial direction. This makes for an optimised amount of edges while keeping the layered structure of MoS$_2$, which seems to be responsible for the photon absorbing properties in the bulk material. These nanotubes should ideally not be very long. In this design both the semiconducting and electrocatalytic property of MoS$_2$ is used to make the photoelectrocatalyst. (b) This shows a Si or other semiconducting material pillar onto which MoS$_2$ nanoplatelets are attached with the basal plane perpendicular to the pillars. This optimises the conduction from the light harvesting Si through the conducting sheet to the active edges. This design uses the electrocatalytic properties of the MoS$_2$ and the semi-conducting properties of the Si. Blue spheres indicate molybdenum and yellow spheres indicate sulfur.

which are around 2200 times more conductive than across the layers. The second design shows Si or some other semi-conducting material, pillars onto which MoS$_2$ nanoplatelets are attached with the basal plane perpendicular to the pillars. This optimises the conduction from the light harvesting Si through the conducting sheet or along the conducting edges to the active edge sites. The number of platelets should be as large as possible and their size as small as possible. It should be noted that due to the similarity of the MWMoS$_2$@MWCNT composite and the nanotubes in Fig. 11(a), the MWMoS$_2$@MWCNT composite was also investigated for the photoelectrocatalytic HER activity, but no activity could be detected. This is likely due to (i) the material not being p-type, or (ii) a high absorption of the light in the carbon paper electrode and the MWCNTs, or possibly both.

It is generally seen that the field of the electrochemical HER using MoS$_2$ has been experiencing a renaissance in recent years, adding to the hope that a viable solution for renewable hydrogen production may be achieved in the future. Naturally, the majority of sustainable energy in the future will be produced as electricity and be used immediately. However, the demand for storage increases simultaneously in order to meet the need for a flexible and continuous energy production. This storage could be achieved through renewable hydrogen production either by electrolysis or by producing hydrogen directly from sunlight. A great deal of effort has been put into realising this using a variety of materials and designs; only the future will tell which is the best.

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References
