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$CuIn_xGa_{1-x}Se_2$ as an efficient photocathode for solar hydrogen generation

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ABSTRACT

Utilizing the energy in the sun to efficiently split water into hydrogen and oxygen can have a huge beneficial impact on a future post-carbon energy system. There is still, however, some way to go before this concept will be fully competitive. At the heart of the problem is finding and designing materials that can drive the photoreaction in an efficient and stable way. In this work we demonstrate how CIGS ($CuIn_xGa_{1-x}Se_2$), can be used for photo reduction of water into hydrogen. CIGS, which is a proven good solar cell material, does not in itself have the appropriate energetics to drive the reaction to any larger extent. Here we show that by utilizing a solid state pn-junction for charge separation and a catalyst deposited on the surface, the efficiency is significantly improved and photocurrents of 6 mA/cm^2 are demonstrated for the reduction reaction in the configuration of a photoelectrochemical cell. The stability of CIGS in water under illumination turns out to be a problem. In our present set-up, we demonstrate that separation between the charge carrier generation, which takes place in the solar cell, from the catalysis, which takes place in the electrolyte leads to improved stability, while keeping the essential functions of the processes. By incorporating appropriate charge separation layers and optimizing the catalytic conditions at the surface of the electrodes, photocurrents in excess of 20 mA/cm^2 are reached for the reduction half reaction, demonstrating how essentially the full potential of CIGS as an efficient absorber material can be utilized in photocatalytic reduction of water into hydrogen.

1. Introduction

Solar water splitting is a process, where energy in sunlight is converted into chemical energy in molecular hydrogen and could, if made efficiently enough, be a vital part in a future post-petrochemical energy system. Hydrogen could be produced as a fuel for the transport sector and as feedstock for the industry. It also has a value for temporary storage of energy in a system based on intermittent sources such as wind and photovoltaics. There is, however, still a long way to go until these concepts leave the research facilities and could compete on the open markets. To get there is to a large extent

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a problem of materials and how the materials are applied. Since the Fujishima and Honda article on water splitting in 1972 [1] using TiO_2, extensive research has been devoted towards finding suitable materials that could drive the photoreaction. In a review from 2008 Osterloh lists over 130 different materials, mostly oxides, which to different extents have been investigated for this purpose [2]. To our knowledge, no single material capable of driving the complete water splitting reaction to a level which is technologically relevant has been demonstrated.

Given the material requirements, the electrical potential needed and the spectrum of the sunlight at the surface of the Earth, it may very well be that no material exists that on its own can drive the reaction efficiently enough. A working device must include a good solar light absorber. The band gap must be large enough for the generated charge carriers to have enough overpotential to drive both the oxidation and the reduction reaction. The position of the band edges must match the oxidation and reduction potential of water. The transport properties have to be good in comparison to the dimensions of the material and it has to be stable in water under solar illumination. It is also beneficial if the material is cheap, abundant and nontoxic. The material requirements are thus basically the same as for good solar cell materials, but with a set of additional hard constraints.

A potentially beneficial approach to cope with this set of material requirements is to construct a device consisting of several different materials. It is then the device as a whole instead of the individual components, which needs to fulfill the full set of constraints mentioned above. This opens for new possibilities for handling the problem. By separating and dividing the functions between different materials some promising results have been achieved like the 16% efficient device based on GaAs and GaInP from Turner et al. [3,4] and the "artificial leaf" from Nocera [5,6]. Even these state-of-the-art concepts do however suffer from problems with stability and efficiency. The search for suitable material combinations and ingenious device concept thus continues.

In this paper we investigate the possibilities to use CIGS ($CuIn_xGa_{1-x}Se_2$), which is a proven efficient solar cell material, for solar water splitting applications. Solar cells based on CIGS made with thin film technologies currently have a world record efficiency of 20.3% [7], and have reached the commercial domain, though still with a rather low share of the global PV-market. CIGS is a highly interesting candidate material for solar hydrogen production both because of its proven high efficiency as a solar cell material but also because the conduction band is well positioned with respect to the reduction potential of water. Given this, surprisingly few reports are found in the literature dealing with CIGS in a water splitting context. There is one article from Neumann et al. [8] who have made a membrane of TiO_2/Ti/Mo/CIGS/CdS/NbTiO/Pt where they obtain hydrogen evolution and while using sacrificial agents reach up to 1% external quantum efficiency. Valderrama et al. [9] have made a short investigation on CIGS as a photo-anode and demonstrated a 0.3 V shift between the dark and the light characteristics. Yokoyama et al. [10] have shown that charge separation is a potential problem, and demonstrate some interesting photocurrents but with no specification of incident light intensity. We have also found two articles investigating $CuGaSe_2$ reporting some promising photocurrents [11,12].

The band gap and band edge positions dictate that CIGS will not be able to drive both the oxidation and the reduction by itself, which is identical to the situation for other, more thoroughly studied systems like Fe_2O_3 [13], Cu_2O [14] and WO_3 [15]. The CIGS electrode will here be used as photocathode for the hydrogen production, and has to be combined with a photo-anode for the other half reaction in order to be able to construct a stand-alone device for unassisted water splitting.

In this paper we demonstrate how CIGS can be used as an efficient photocathode for water reduction if proper consideration to the charge separation and transfer is taken into account. In a classical photo-electrochemical cell (PEC) configuration, photocurrents up to 6 mA/cm^2 are demonstrated. CIGS does however show a tendency to be unstable in water under illumination, just like other efficient materials.

Here we also compare the PEC configuration to a PV-electrolysis system using a CIGS device with the same structure. This allows separation of the light absorption process, which takes part in the solar cell, from the catalysis process, which takes part in the electrolyte and thereby avoiding the stability problem. We argue that the main difference between the two concepts is the difference in the distance of charge transport which increases from the micrometer range to the centimeter range. We also argue that this should be considered a small change considering the fundamental function of the light to hydrogen process and that it opens up possibilities for optimization. It also facilitates direct comparison between the PEC and the PV-electrolysis, considering area needs for full deployment in hydrogen production. By changing the catalytic conditions around the electrode we demonstrate stable photocurrents in order of 20 mA/cm^2 for an electrolysis setup. We also discuss the different approaches with respect to the underlying physics, the efficiencies as well as the comparative advantages and drawbacks.

2. Theory

The problem of solar water splitting can basically be divided into four different functions in which the device needs to perform well. Light must be absorbed and charge carriers have to be generated at an energetically favorable chemical potential for the reaction. The photo-generated charge carriers have to be separated before they recombine. They further need to be transported to the semiconductor–electrolyte interface (SEI). Finally there must be an energetically favorable pathway for the desired reaction at the SEI, which means high catalytic activity. In addition to this, the device has to be stable for a long time, and it is also highly preferable if it is made of cheap, abundant and nontoxic components. The functions of a water splitting device can be specified as products in an expression for the external quantum efficiency (EQE) by equation (1),

$$\mathrm{EQE}(\lambda) = \mathrm{LHE}(\lambda)\cdot\Phi_{\mathrm{sep}}\cdot\Phi_{\mathrm{trans}}\cdot\eta_{\mathrm{cat}} \quad (1)$$

where LHE(λ) is the light harvesting efficiency as a function of wavelength, Φ_{sep} is the quantum efficiency for charge separation with respect to geminate recombination, Φ_{trans} is the