Abstract: Splitting of water into hydrogen and oxygen molecules using sunlight is an attractive method for solar energy storage. Until now, photoelectrochemical hydrogen evolution is mostly studied in acidic solutions where the kinetics for hydrogen evolution is more facile than in alkaline solutions. Herein, we report photoelectrochemical hydrogen production in alkaline solutions, which are more favorable than acidic solutions for the complementary oxygen evolution half reaction. We show for the first time that amorphous molybdenum sulfide is a highly active hydrogen evolution catalyst in basic medium. The amorphous molybdenum sulfide catalyst and a Ni-Mo catalyst are then deposited on surface-protected cuprous oxide photocathodes to catalyze sunlight-driven hydrogen production in 1 M KOH. The photocathodes give photocurrents of -6.3 mA cm\(^{-2}\) at the reversible hydrogen evolution potential, the highest yet reported for a metal oxide photocathode using an earth-abundant HER catalyst.

The splitting of water using sunlight energy in a photoelectrochemical (PEC) cell is a promising method to produce renewable hydrogen.\(^{[1-2]}\) The water splitting process is made of two half-reactions: the hydrogen evolution reaction (HER: \(2\text{H}^+ + 2e^- \rightarrow \text{H}_2\)) at the cathode and the oxygen evolution reaction (OER: \(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-\)) at the anode. Because of the high overpotential loss for the OER tends to be several-fold higher than for the HER when state-of-the-art electrocatalysts are applied, the efficiency of PEC water splitting should be higher in basic medium than in acidic medium. Furthermore, in basic solutions a number of abundant and inexpensive metal oxide catalysts exhibit comparable and even higher OER activity than rare and expensive RuO\(_x\) and IrO\(_x\) catalysts, whereas in acidic solutions only RuO\(_x\) and IrO\(_x\) are good catalysts.\(^{[4-6]}\) With more desirable OER catalysts available for use in alkaline solutions, we were therefore motivated to develop photocathodes capable of efficiently evolving hydrogen in basic medium. These photocathodes might then be combined with either a solar cell or a photoanode to obtain a tandem device for unassisted water splitting in alkaline solutions. Significant progress has been made in PEC hydrogen evolution in acidic and even neutral solutions,\(^{[7-11]}\) however, to the best of our knowledge, only CaFe\(_2\)O\(_4\) has been reported as a photocathode for PEC hydrogen evolution in alkaline solutions.\(^{[12]}\) However, the efficiency of solar energy conversion was very low as the incident photon to current conversion efficiency (IPCE) in the visible light region was below 5%. Herein, we show that amorphous molybdenum sulfide and Ni-Mo catalysts can be coupled to surface protected Cu\(_2\)O photocathodes to produce hydrogen in alkaline solutions with efficiency comparable to analogous devices in acidic solutions.

We have recently shown that electrochemically deposited amorphous molybdenum sulfide films are an active hydrogen evolution catalyst.\(^{[13-16]}\) The catalyst is more active in acidic solutions than in neutral and slightly basic solutions.\(^{[17]}\) We reported that different electrochemical deposition methods gave precatalysts that are composed of different proportions of amorphous MoS\(_3\) and MoS\(_2\), yet during hydrogen evolution, all precatalysts were converted into the same active species MoS\(_{2+x}\).\(^{[15]}\) While examining the activity of the catalyst in alkaline solutions, we noticed that different precatalysts had drastically different stability in 1 M KOH. If the precatalyst contains MoS\(_3\), then it is quickly dissolved in the electrolyte. If the precatalyst contains no MoS\(_3\), then it is stable in 1 M KOH. Fig. S1 and Supporting Movie 1 show the results of treating two precatalysts on fluoride-doped tin oxide (FTO) with 1 drop of 1 M KOH. The MoS\(_2\)-AE film was deposited by constant anodic electrolysis (AE) and contains mainly amorphous MoS\(_2\). Upon contact with the KOH solution, this film quickly delaminated from the FTO and was dissolved in a few seconds. The MoS\(_{2+x}\)-CE film was deposited by constant cathodic electrolysis (CE) and contains already the active MoS\(_{2+x}\) catalyst but not MoS\(_3\). This film is stable in 1 M KOH solution.
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b) Figure 1. a) Linear sweep voltammetry (from positive to negative) of MoS$_{2+x}$-CE/FTO and Ni-Mo/FTO. b) Linear sweep voltammetry (from positive to negative) of MoS$_{2+x}$-CE/Ni foam and Ni-Mo/Ni foam. Conditions: 1 M KOH (pH 13.6), scan rate: 1 mV s$^{-1}$, iR drop corrected, the 5th linear sweep is shown.

Fig. 1a shows the HER activity of the MoS$_{2+x}$-CE catalyst (loading: 20 µg cm$^{-2}$) on FTO in 1 M KOH. The overpotential for a current density of 10 mA cm$^{-2}$ is about 310 mV. In comparison, the same electrode reaches 10 mA cm$^{-2}$ at $\eta$ = 235 mV in 1 M H$_2$SO$_4$. Fig. S2 (supporting information) shows that the HER activity of MoS$_{2+x}$-CE is stable during 10 hours. Although amorphous molybdenum sulfides and MoS$_2$ nanoparticles are by now well-established HER catalysts in acidic solutions, [14, 16-19] this is the first time they are shown as active and stable HER catalysts in basic solutions.

Recently, Mo$_2$C, [20] MoB, [20] and Ni$_2$P [21-22] nanoparticles were reported as good HER catalysts in basic solutions. The activity of MoS$_{2+x}$-CE catalyst is similar to those catalysts, and higher than NiO$_x$ and Ni(OH)$_2$ films (Table S1; supporting information). Ni-Mo is reported as one of the most active HER catalysts in alkaline solutions. [23] Fig. 1a shows the HER activity of Ni-Mo on FTO in 1 M KOH. The Ni-Mo/FTO electrode was prepared by passing a cathodic charge of 4.5 C cm$^{-2}$, corresponding to a catalyst loading of about 15 µg cm$^{-2}$ (see Supporting Information). [24] The Ni-Mo catalyst is more active than MoS$_{2+x}$ and requires an overpotential of 200 mV to reach 10 mA cm$^{-2}$. Both the MoS$_{2+x}$ and Ni-Mo catalysts can be deposited on high surface area substrates such as Ni foam to give high current densities at modest overpotentials. Fig. 1b shows that MoS$_{2+x}$ on Ni foam reaches 10 mA cm$^{-2}$ at $\eta$ = 210 mV, and 100 mA cm$^{-2}$ at $\eta$ = 335 mV overpotential. Ni-Mo on Ni foam reaches 10 mA cm$^{-2}$ at $\eta$ = 150 mV, and 100 mA cm$^{-2}$ at $\eta$ = 280 mV overpotential. Fig. S3, supporting information shows that the Faradaic yield for HER is close to 100% for the MoS$_{2+x}$-CE catalyst.

Figure S4, supporting information shows the Tafel plot for the MoS$_{2+x}$-CE and Ni-Mo catalysts. For the MoS$_{2+x}$-CE catalyst, the Tafel slope is 84 mV dec$^{-1}$ in 1 M KOH but 39 mV dec$^{-1}$ in 1 M H$_2$SO$_4$. In comparison, the Ni-Mo catalyst has a Tafel slope of 119 mV dec$^{-1}$ at modest overpotentials.

Because the MoS$_{2+x}$ and Ni-Mo catalysts can be electrochemically deposited under mild conditions, they are attractive HER catalysts to integrate with a photocathode for PEC hydrogen production in alkaline solutions. The photocathode we chose is surface-protected $p$-type Cu$_2$O. Cu$_2$O is a promising low-cost material with a direct bandgap of 2.0 eV. The material is suitable for capturing a large fraction of sunlight with a maximum theoretical solar-to-hydrogen (STH) efficiency of 18% under AM 1.5 G solar illumination. Efficient PEC hydrogen production has been achieved on surface-protected Cu$_2$O using Pt, RuO$_x$, and MoS$_{2+x}$ as HER catalysts, but only in acidic and near-neutral solutions. [25-27]

The protected $p$-Cu$_2$O photoelectrodes, Cu$_2$O/AZO/TiO$_2$, were prepared as previously described. [25, 27] Following cathodic electrodeposition of Cu$_2$O, atomic layer deposition was used to apply a thin layer of aluminum-doped zinc oxide (AZO, 20 nm) to create a $p$-$n$ junction with Cu$_2$O, and a layer of titanium oxide (TiO$_2$, 100 nm) was applied to protect the photovoltaic junction from the electrolyte solution. The MoS$_{2+x}$ and Ni-Mo catalysts were deposited on the TiO$_2$ layer photoelectrochemically (Fig. S5, supporting information). Fig. 2 shows Scanning Electron Microscopy (SEM) images of the top and cross section of the catalyst-coated Cu$_2$O photocathodes. XPS analysis of the as-prepared photocathodes show that both catalysts were deposited conformally on the surface (Fig. S6, supporting information). The Mo:S ratio in the MoS$_{2+x}$ is 1:1.7; the Ni to Mo ratio in Ni-Mo is 85:15, similar to values found in the literature. [24]

The MoS$_{2+x}$ film has a thickness of 30-50 nm, while the Ni-Mo film has a thickness of about 40 nm. Compared with Ni-Mo, the MoS$_{2+x}$ film appeared rougher. Estimation of the catalyst loading from the total charge passed during photoelectrodeposition is complicated by the concomitant photoelectrochemical hydrogen evolution.
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The catalyst-coated p-Cu2O photocathodes were tested for hydrogen evolution under simulated AM 1.5 G (100 mW cm\(^{-2}\)) solar illumination in 1 M KOH. Fig. 3a displays the current-potential curves in the dark and under illumination. The onset potential of photocurrent (\(j = -0.1\) mA cm\(^{-2}\)) is +0.48 V vs. RHE for the MoS\(_{2+x}\)/Cu2O photocathode, similar to the onset potential of an analogous photocathode at pH = 1.0\([27]\). A photocurrent of -6.3 mA cm\(^{-2}\) was obtained at 0 V vs. RHE, which is even higher than the photocurrent at pH 1.0 (-5.7 mA cm\(^{-2}\)). Much lower photovoltage and photocurrents were obtained on the same photocathode at pH 7.0, indicating the influence of pH. Dark currents were negligible. The onset potential of photocurrent (\(j = -0.1\) mA cm\(^{-2}\)) is +0.53 V vs. RHE for the Ni-Mo/Cu2O photocathode. The more positive onset potential obtained with the Ni-Mo catalyst is consistent with its higher HER activity than MoS\(_{2+x}\). Interestingly, the current densities at potentials negative of 0.45 V are nearly identical for the MoS\(_{2+x}\)/Cu2O and Ni-Mo/Cu2O photocathodes. Thus, at 0 V vs. RHE, the Ni-Mo/Cu2O photocathode also gives a current density of -6.3 mA cm\(^{-2}\). At this moment, it is unclear why the Ni-Mo catalyst gives a more positive onset potential but identical photocurrent densities at more negative potentials than the MoS\(_{2+x}\) catalyst. Electrochemical impedance spectroscopy will be applied to dissect the complex photoelectrochemical process. Fig. 3b shows that the MoS\(_{2+x}\)/Cu2O photocathode has a quantitative Faradaic yield for hydrogen production.

The long term stability of the MoS\(_{2+x}\)/Cu2O and Ni-Mo/Cu2O photoelectrodes in 1 M KOH was evaluated under continuous AM 1.5 illumination at 0 V vs. RHE. The photocurrents of both photoelectrodes decayed gradually over 10 hours. The stability of these photoelectrodes is higher than an analogous MoS\(_{2+x}\)/Cu2O photocathode at pH 1.0, where the TiO\(_2\) protective layer was dissolved and the photocathode lost completely its activity after 8 h (Fig. S7, supporting information). The deactivation of the devices in 1 M KOH is not due to the dissolution of the TiO\(_2\) layer as in acidic solutions, but due to the formation of Ti\(^{3+}\) traps in TiO\(_2\), evidenced by the darkening of the protective film after prolonged testing (Supporting Movie 2).

Increasing the photovoltage generated by the buried p-n junction and improving the HER activity of the catalyst layer should enhance the extraction of photoexcited electrons for hydrogen production, thereby decreasing the trapping of electrons in the TiO\(_2\) layer. This in turn should lead to higher stability.

![Figure 2.](image)

**Figure 2.** a) SEM image of the surface of a MoS\(_{2+x}\)/Cu2O photoelectrode. b) SEM image of the surface of a Ni-Mo/Cu2O photocathode. c) SEM image of the cross section of a MoS\(_{2+x}\)/Cu2O photoelectrode. d) SEM image of the cross section of a Ni-Mo/Cu2O photocathode. Scale bar: 200 nm.

![Figure 3.](image)

**Figure 3.** PEC performance of photocathodes in 1 M KOH. a) Current-potential curve for surface protected photocathode activated for HER with MoS\(_{2+x}\) and Ni-Mo catalysts. MoS\(_{2+x}\)-CE/Cu2O pH 7.0 is also shown. b) Faradaic efficiency for a MoS\(_{2+x}\)-CE/Cu2O photocathode biased at 0 V vs. RHE. The volume of hydrogen produced during 130 minutes of illumination was measured using a gastight, home-made H cell calibrated for pressure and gas quantification.

In summary, we show for the first time that amorphous molybdenum sulfide is an active and stable hydrogen evolution catalyst in alkaline solutions. The molybdenum sulfide catalysts and a Ni-Mo catalyst are integrated onto surface-protected Cu2O photocathodes. These catalyst-coated Cu2O photoelectrodes exhibit high photoelectrochemical activity for hydrogen evolution in alkaline solutions. Photocurrents as high as -6.3 mA cm\(^{-2}\) have been obtained at 0 V vs. RHE, which would correspond to 7.7% STH efficiency in a tandem cell where the bias is provided.
by a second photocative component. The photoelectrochemical hydrogen evolution has a quantitative Faradaic yield. Even though the Ni-Mo catalyst is a better electrocatalyst than MoS_{2+x} in alkaline solutions and gives a slightly more positive onset potential for hydrogen evolution for the p-CuO_{2} photoelectrode, the photocurrent densities are identical at potentials more negative than 0.45 V vs. RHE. The devices reported here are the first highly active photocathodes in alkaline solutions that make use of earth-abundant HER catalysts and inexpensive photoabsorbers. The development of these devices offers a new opportunity for efficient solar water splitting in basic medium.

Experimental Section

The conditions for the electrochemical and photoelectrochemical deposition of amorphous molybdenum sulfide films on conductive substrates and surface protected CuO have been previously reported by our group.\[15, 27\] In brief, electrochemical deposition was done from a freshly prepared 2 mM ammonium tetramethylammonium solution ([NH_4]_2MoS_4, Aldrich, 99.97%) in 0.1 M NaClO_4 (ABCr, 99%). Different potentials were used to prepare the different electrodes. MoS_{2+x}-CE was deposited on TEC-15 fluorine-doped tin oxide (FTO; Nippon Sheet Glass) and Ni Foam (95% porosity, Goodfellow Cambridge Limited) substrates by constant potential electrolysis at -0.3 V vs. RHE for 1 h. MoS_{2+x}-AE was deposited by constant potential electrolysis at 0.7 V vs. RHE for 1 h and MoS_{2+x}-CV was deposited by cyclic voltammetry between -0.4 and 0.7 V vs. RHE at a scan rate of 50 mV s^{-1} (50 cycles). The photoelectrodeposition of MoS_{2+x}-CE on surface protected CuO was carried out under simulated AM 1.5 G solar illumination (1 sun) in a 0.2 mM (NH_4)_2MoS_4, 0.1 M NaClO_4 solution at a constant potential of 0.2 V vs. RHE. The PEC deposition time was typically 50 min.

The nickel molybdenum (Ni-Mo) catalyst was deposited on FTO and Ni foam by electrochemical deposition. The nickel foam was pretreated by dipping for 1 min in 6M HCl in order to increase the hydrophilicity of the foam by electrochemical deposition. The nickel foam was pretreated by a second photoactive component. The photoelectrochemical hydrogen evolution has a quantitative Faradaic yield. Even though the Ni-Mo catalyst is a better electrocatalyst than MoS_{2+x} in alkaline solutions and gives a slightly more positive onset potential for hydrogen evolution for the p-CuO_{2} photoelectrode, the photocurrent densities are identical at potentials more negative than 0.45 V vs. RHE. The devices reported here are the first highly active photocathodes in alkaline solutions that make use of earth-abundant HER catalysts and inexpensive photoabsorbers. The development of these devices offers a new opportunity for efficient solar water splitting in basic medium.

Keywords: water splitting • photoelectrochemistry • photocatalysis • hydrogen evolution • cuprous oxide

References

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Amorphous molybdenum sulfide and nickel-molybdenum alloy catalyze efficient photoelectrochemical hydrogen evolution on a cuprous oxide photocathode in alkaline solutions.

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