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Engineering Cu$_2$O/NiO/Cu$_2$MoS$_4$ Hybrid Photocathode for H$_2$ Generation in Water

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Abstract

We report a scalable process for fabricating a multiple-layer hybrid photocathode, namely Cu$_2$O/NiO/Cu$_2$MoS$_4$, for H$_2$ generation in water. In pH 5 solution and under 1 Sun illumination, the photocathode showed interesting photocatalytic properties. The onset photocurrent was recorded at +0.45 V vs. RHE while at 0 V vs. RHE, photocurrent density of 1.25 mA.cm$^{-2}$ was obtained. It was found that NiO interlayer enhances charge transfer from Cu$_2$O light harvester to Cu$_2$MoS$_4$ hydrogen evolution reaction electrocatalyst which in turn accelerates charge transfer at the electrode/electrolyte interface and therefore improve photocatalytic properties of the Cu$_2$O photocathode.
Main Text

Solar-induced water splitting is considered as a promising technology to harvest abundant but intermittently available solar energy and convert it into chemical energy stored within the H₂ molecule.¹,² Recent theoretical calculations have shown that solar-to-hydrogen conversion efficiencies up to 28-30% can be expected³,⁴ that is just matching well with the US Department of Energy’s target. However, to achieve this efficiency, key challenges remain in searching for viable materials to engineer appropriate photoelectrodes which can be then assembled within a complete highly efficient bias-free photoelectrochemical cell (PEC).

\[ 2H^+ + 2e^- \rightarrow H_2 \]  (eq. 1)

\[ \text{Cu}_2\text{O} + 2\text{H}^+ + 2e^- \rightarrow 2\text{Cu} + \text{H}_2\text{O} \]  (eq. 2)

\[ 2\text{CuO} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cu}_2\text{O} + 2\text{OH}^- \]  (eq. 3)

Among available materials being considered for engineering photocathode, copper (I) oxide (Cu₂O) appears to be a promising candidate thanks to its visible light absorption properties (band gap of about 2.1 eV), abundance and its appropriate conduction band which provides sufficiently large reductive electrochemical potential upon illumination to drive the catalytic hydrogen evolution reaction (HER, eq. 1).⁵ However, the main drawback of Cu₂O is its self-reduction (to Cu, eq. 2) and self-oxidation (to CuO, eq. 3) potentials lying within the band gap.⁵ To limit the self-reduction process, it is critical to drive photo-generated electrons to Cu₂O electrode surface and use these electrons for the HER in an efficient manner.⁵,⁶ Due to the low kinetic of the HER on the pristine Cu₂O electrode surface, employing an HER electrocatalyst as co-catalyst is needed.¹,²,⁷

Indeed, the best electrocatalyst for the HER is platinum, which is therefore a judicious choice of co-catalyst for constructing hybrid photocathode for the H₂ generation.⁵ However, employing platinum or other precious elements may not be the most economical solution to realize cost-effective photoelectrodes/photoelectrochemical cells. Moreover, unlike low conduction band semiconductors e.g. TiO₂ (E_{CB} = -0.17 V vs. RHE (Reversible Hydrogen Electrode)) wherein using an extremely active electrocatalyst functioning with very low overpotential e.g. Pt (η ~30mV) is needed, a larger choice of HER co-catalysts can be applied for semiconductors having more reductive conduction band such as Si, CdS.⁸-¹² Cu₂O has conduction band positioned at potential about -0.7 V vs. RHE.¹³ Hence, in principle
numerous HER electrocatalysts can be used as co-catalyst to promote the H₂ generation on Cu₂O surface electrode.

Recently, sulfides of transition metals e.g. (Mo/W)(S/Se)$_2$, Co(S/Se) have gained great attention as low-cost, potential electrocatalysts for the H₂ generation in water.$^{14-19}$ Employing MoS$_2$ co-catalyst to enhance photocatalytic activities of diverse semiconducting photocatalysts/ photoelectrodes has been described.$^{8-10,20,21}$ We have demonstrated hetero-bimetallic sulfides as promising electrocatalysts for the HER in water over wide pH range (pH 0-12) with very good stability and relatively low overpotential requirement of about 130-150 mV.$^{18,19}$ Herein, we report on using of nanopowder copper-molybdenum-sulfide (Cu$_2$MoS$_4$) co-catalyst to promote the H₂ photo-generation on Cu₂O photocathode in water. We found that Cu$_2$MoS$_4$ co-catalyst induced a significant anodic shift of 300 mV of onset potential, together with a significant improved photostability of Cu₂O photocathode.

**Figure 1:** Characterization of as-deposited Cu₂O and hybrid multiple-layer Cu₂O/NiO/Cu$_2$MoS$_4$ electrodes. a) SEM image (top view) of a pristine Cu₂O electrode. b) Cross section analysis of a Cu₂O/NiO/Cu$_2$MoS$_4$ photoelectrode. The NiO interlayer is not visible. c) XRD patterns of Cu₂O (black) and NiO (red) deposited on FTO substrate.

Cu₂O photoactive thin film (thickness of ~2.3 µm) was electrodeposited on clean conductive fluorine-doped tin oxide (FTO) substrate employing an alkaline copper lactate solution, following the preparation process reported by Golden et al.$^{22}$ SEM analysis showed compact morphology with relatively large Cu₂O grains (figures 1a, S1) while XRD analysis revealed crystalline Cu₂O structure with Cu₂O (111) dominant phase (figure 1c). The photoelectrochemical properties of the deposited Cu₂O electrode were then evaluated in a pH
5 Na$_2$SO$_4$ (1M) solution buffered with NaHSO$_4$. A three-electrode-configuration electrochemical cell was employed. The counter electrode was a Pt wire while the reference electrode was an Ag/AgCl 3M KCl. All potential was quoted versus the Reversible Hydrogen Electrode (RHE). Cu$_2$O working electrode having photoactive area of 0.23cm$^2$ was illuminated with standard 1 Sun light source. We adopted back side (FTO side) illumination configuration in order to simulate the best function of the Cu$_2$O-based photocathode in perspective of assembling this photocathode together with an appropriate photoanode to engineer a complete Z-scheme photoelectrochemical cell. Indeed, in a Z-scheme cell, light is expected to illuminate on the photoanode front-site.

![Figure 2: Photoelectrochemical properties of Cu$_2$O-based photocathodes in a pH5 Na$_2$SO$_4$ (1M) solution. a) I-V curves collected under 1 Sun illumination on a pristine Cu$_2$O (curve (ii)), a Cu$_2$O/ Cu$_2$MoS$_4$ (curve (iii)), a Cu$_2$O/ NiO (curve (iv)) and a Cu$_2$O/ NiO/ Cu$_2$MoS$_4$ (curve (v)) photocathode. Without light illumination, these Cu$_2$O-based photocathodes showed similar I-V curves. For clarification, only the curve collected on a Cu$_2$O/NiO/Cu$_2$MoS$_4$ (curve (i)) was presented. b) Generated photocurrent achieved at applied potential of 0V vs. RHE employing a pristine Cu$_2$O (curve (ii)), Cu$_2$O/Cu$_2$MoS$_4$ (iii), Cu$_2$O/NiO (curve (iv)), and a Cu$_2$O/NiO/Cu$_2$MoS$_4$ (curve (v)) photocathode.](image)

As presented in figure 2a (curve (ii)), the pristine Cu$_2$O photoelectrode showed important photocurrent even at low applied bias, from 0 to +0.5 V vs. RHE. In this potential range, a current peak at ca. +0.25 V vs. RHE was observed. Similar phenomenon was found for other
Cu$_2$O photoelectrodes which showed a photocurrent peak at ca. +0.3 V vs. RHE as reported by Paracchino et al.$^{23}$ We note that Parrachino et al. deployed photogenerated current in this positive potential range to quantify the photocatalytic activities of electrodeposited Cu$_2$O photoelectrodes. Indeed, the photogenerated currents at potentials more positive than 0 V vs. RHE are of great interests in the context of application for the solar-hydrogen production if and only if these currents are relevant to the photo-reduction of proton into hydrogen. However, photoelectrolysis at +0.25V vs. RHE employing a 1.5 cm$^2$ Cu$_2$O photoelectrode in a gas-tight closed electrochemical cell showed almost no photogeneration of hydrogen gas as analysed by gas chromatography. Photocurrent-to-hydrogen yield of only 0.54% (figure S2) was calculated for 10 min continuous measurement under 1 Sun illumination. It is consistent with Electrochemical Impedance Spectroscopy (EIS) analysis. Nyquist plot analysis for an illuminated Cu$_2$O electrode hold at +0.3V vs. RHE showed no charge transfer at the Cu$_2$O/electrolyte interface (figure 3, curve (ii)). XRD analysis performed on the Cu$_2$O electrode after photoelectrolysis experiment showed the appearance of Cu metal peaks (figure S3). Therefore, we conclude the photocurrent observed is originated from the self-reduction of Cu$_2$O into Cu metal. Similar zero current-to-H$_2$ yield was recorded by Lin et al. for a Cu$_2$O nanowires electrode at less positive potential of 0V vs. RHE in a pH 6 Na$_2$SO$_4$ solution.$^{24}$
Figure 3: Nyquist plots analysis performed on Cu$_2$O-based photoelectrodes immersed in a pH5 Na$_2$SO$_4$ (1M) solution, at applied bias of +0.3V vs. RHE, under illumination: Cu$_2$O/NiO (curve (i)), Pristine Cu$_2$O (curve (ii)), Cu$_2$O/NiO/Cu$_2$MoS$_4$ (curve (iii)) and Cu$_2$O/Cu$_2$MoS$_4$ (curve (iv)).

A layer of Cu$_2$MoS$_4$ HER electrocatalyst (thickness of ~2.7 µm) was then deposited on surface of the Cu$_2$O electrode, employing a scalable solution process in order to enhance the kinetic of the HER at the Cu$_2$O/ electrolyte interface (figure 1b). To do so, a well-dispersed suspension of Cu$_2$MoS$_4$ nanopowder in water was drop-casted on Cu$_2$O electrode surface, followed by air-drying prior to characterizations. It is worth noting that a back-side illumination on the Cu$_2$O electrodes allows removing visible light absorption effect of the Cu$_2$MoS$_4$ layer decorated. It was found that the Cu$_2$MoS$_4$ strongly absorbs visible light but displays negligible photocatalytic activities (figures S4, S5). EIS analysis showed enhanced charge transfer at the Cu$_2$O/Cu$_2$MoS$_4$ electrode surface interfaced with electrolyte solution compared with that observed for the pristine Cu$_2$O/ electrolyte interface, thus clearly evidenced the electrocatalytic role of the deposited Cu$_2$MoS$_4$ layer (figure 3, curves (ii) and (iv)). Nyquist plot collected at potential +0.3V vs. RHE on the illuminated Cu$_2$O/Cu$_2$MoS$_4$ displayed two semicircles. We attributed the first semicircle to the electron transfer from Cu$_2$O conduction band to Cu$_2$MoS$_4$ electrocatalyst while the second semicircle is attributed to the electron injection from Cu$_2$MoS$_4$ to the electrolyte, which induces the H$_2$ evolution. However, the Cu$_2$O/Cu$_2$MoS$_4$ electrode showed low photostability. The photogenerated current was found to rapidly decrease with time, as observed for a pristine Cu$_2$O electrode without Cu$_2$MoS$_4$ co-catalyst decoration (figure 2b, curves (ii) and (iii)). We tentatively attribute this instability to the fact that the porosity of the Cu$_2$MoS$_4$ layer is permeable to protons that causes the photocorrosion of Cu$_2$O (eq. 2). It suggests that a more efficient protective layer placed in between Cu$_2$O light harvester and Cu$_2$MoS$_4$ electrocatalyst layer is required.

For such interlayer purpose, we have chosen NiO material. Indeed, NiO has a large band gap of about 3.6 eV and thus does not absorb visible light. It has been shown to be an effective protective layer for Cu$_2$O nanowires photocathode. We deposited NiO layer on Cu$_2$O electrode surface employing method described by Lin et al with some slight modification (refer SI for details). The thickness of NiO layer was controlled by varying number of deposition cycles (N= 1-5). Each NiO deposition cycle refers to spin-coating a volume of 50
\( \mu \text{L} \) solution of 0.5M Ni(OAc)\(_2\) precursor in 2-methoxyethanol onto geometrical 2.25cm\(^2\) Cu\(_2\)O electrode, followed by annealing at 220\(^\circ\)C in air for 30 min. Elemental analysis performed on a Cu\(_2\)O/ NiO (N=2) by Energy Dispersive X-ray Spectroscopy (EDX) showed Cu, O and Ni elements (figure S6), thus suggesting production of NiO layer on Cu\(_2\)O surface after above treatment with Ni(OAc)\(_2\) precursor. However, attempts to quantify the thickness of deposited NiO layer on Cu\(_2\)O via SEM cross section analysis were unsuccessful, likely due to the rough Cu\(_2\)O electrode surface and the thin NiO layer. To overcome this problem and make sure the deposited material from Ni(OAc)\(_2\) precursor was indeed the expected NiO, we performed control deposition on smooth FTO substrate. NiO film with a thickness of 156 nm was deposited by repeating 10 deposition cycles (N=10) (figure S7). XRD analysis of this film clearly confirmed deposition of crystalline NiO (figure 1c). Assuming a uniform growth, an average growth rate was estimated to be around 16 nm per deposition cycle.

We then aimed to optimize the thickness required for the NiO to protect the Cu\(_2\)O photoelectrode. As shown in figures 2a and S8, the photocurrent peak at +0.25V vs. RHE corresponding to the photocorrosion of Cu\(_2\)O was decreased upon depositing one cycle of NiO (~16nm thickness). The best protective effect was achieved after 2 cycles of NiO treatment. The obtained Cu\(_2\)O/ NiO (~32nm) displayed onset potential at +0.15V vs. RHE for the photocurrent generation. Cu\(_2\)O treated with thicker NiO film showed slightly lower photogenerated current even the same onset potential was recorded. That is likely due to the low conductivity of thick NiO film. As further illustration, photoelectrolysis at 0 V vs. RHE under 1 Sun illumination employing an untreated Cu\(_2\)O photocathode showed a fast decreased photocurrent (figure 2b, curve (ii)), while significantly more stable photocurrent was recorded for a Cu\(_2\)O/NiO (~32nm) photocathode (figure 2b, curve (iv)).

Decorating Cu\(_2\)MoS\(_4\) electrocatalyst on Cu\(_2\)O/NiO (~32nm) electrode benefits from the stability improvement achieved with the NiO layer, resulting in further significant improvement of photoelectrochemical properties. An onset photocurrent shifting to anodic direction of 0.3V was recorded with employing Cu\(_2\)MoS\(_4\) electrocatalyst (figure 2a, curve (v) versus curve (iv)). That is thus among the most effective potential shifting ever recorded for an electrocatalyst decorated on a photocathode surface.\(^5\,8,\,26\) We note that for the purpose of engineering a complete Z-scheme photoelectrochemical cell for solar-induced water splitting by assembling appropriate photoanode and photocathode, each value of onset potential shifting to anodic direction for the photocathode and to cathodic direction for the photoanode is valuable. The hybrid photocathode Cu\(_2\)O/NiO/Cu\(_2\)MoS\(_4\) displayed onset photocurrent...
potential at +0.45V vs. RHE, thus comparable to that reported by Parrachino et al. for the multiple-layers Cu$_2$O/ZnO/TiO$_2$/Pt photocathode.\cite{parrachino5, parrachino23} At constant holding potentials of 0V and +0.3V vs. RHE, our Cu$_2$O/NiO/Cu$_2$MoS$_4$ photocathode generated stable photocurrent, suggesting a good photostability (figures 2b and S9). These generated cathodic photocurrents have origin from the light harvesting properties of the Cu$_2$O absorber since control experiments performed under identical conditions employing a NiO/Cu$_2$MoS$_4$ photoelectrode showed negligible anodic photocurrent (figure S5). Furthermore, in very sharp contrast with the case of pristine Cu$_2$O discussed above, photocurrent generated on the Cu$_2$O/NiO/Cu$_2$MoS$_4$ photocathode at +0.3V vs. RHE has important contribution from the photoreduction of proton into H$_2$. Photocurrent-to-H$_2$ yield of about 31.2% was calculated for this case, on basis of 10 min photoelectrolysis. This performance is also higher than that achieved when employing a Cu$_2$O/NiO (N=2) photocathode without decorating Cu$_2$MoS$_4$ co-catalyst. At applied potential of 0V vs. RHE, faradic current efficiency of 23.1% was calculated (figure S2). We note that these current efficiencies are close to that previously reported by Lin et al. for a Cu$_2$O/NiO photocathode in pH 6 solution (at E$_{appl}$ = 0V vs. RHE, faradic efficiency of 32±6% was calculated on basis of 15 min photoelectrolysis).\cite{lin24} However, bulk photo-electrolysis for longer time showed decreased Faradic current efficiency (figure S2). It indicates photocorrosion process still occurred together with the H$_2$ evolution when the current Cu$_2$O-based photocathodes are used.

Even though the NiO interlayer was not able to totally suppress the photocorrosion of Cu$_2$O, its positive contribution to improve the photostability and photocatalytic activities of the Cu$_2$O photocathode was clearly evidenced. EIS analysis explains the role of NiO interlayer on performance improvement. The lower frequency arc obtained in the Nyquist plot, which is attributed to the charge transfer from the Cu$_2$MoS$_4$ to the solution, is not significantly affected by the NiO interlayer: similar arc resistances are obtained in the fitting of both Cu$_2$O/Cu$_2$MoS$_4$ (2617 Ω) and Cu$_2$O/NiO/Cu$_2$MoS$_4$ systems (2781 Ω) as seen in figure S10 and table S1. However, the interlayer of NiO diminishes the higher frequency arc (651 Ω for Cu$_2$O/Cu$_2$MoS$_4$ and 211 Ω for Cu$_2$O/NiO/Cu$_2$MoS$_4$), which indicates a better charge injection from Cu$_2$O to Cu$_2$MoS$_4$. This improvement has probably its origin in the energetic tuning of the interface: the p-type doping properties of the deposited NiO thin layer revealed by X-ray photoelectron spectroscopy (XPS) (figure S11) can modify the band alignment, generating a favourable band bending for the charge injection. Similar effects have been
reported in other kind of devices where thin layers of NiO improved the electrical behavior of the interfaces despite its low conductivity.\textsuperscript{27}

To sum up, we reported herein scalable fabrication of a promising hybrid photocathode for solar-induced H\textsubscript{2} generation in water. The photoelectrode Cu\textsubscript{2}O/NiO/Cu\textsubscript{2}MoS\textsubscript{4} was made of only earth-abundant-elements and thus represents an attractive example of noble-metal free photocatalytic material. The NiO interlayer was found to enhance charge transfer from light harvester Cu\textsubscript{2}O to Cu\textsubscript{2}MoS\textsubscript{4} electrocatalyst whose incorporation accelerates charge transfer cross photoelectrode/ electrolyte interface and therefore enhances the photocatalytic activities of Cu\textsubscript{2}O for the H\textsubscript{2} generation. Spin coating method adopted in this work can be also easily applied to incorporate NiO interlayer and Cu\textsubscript{2}MoS\textsubscript{4} electrocatalytic layer in other photocathode systems.

We note that our hybrid photocathode Cu\textsubscript{2}O/NiO/Cu\textsubscript{2}MoS\textsubscript{4} is still less effective than the best copper-based multiple-layers photocathode reported by Paracchino et al.\textsuperscript{5} At 0V vs. RHE, a photocurrent of $\sim$1.25 mA.cm\textsuperscript{-2} was recorded for the Cu\textsubscript{2}O/NiO (32 nm)/Cu\textsubscript{2}MoS\textsubscript{4} photocathode which is about 6 times lower than that achieved for the Cu\textsubscript{2}O/ZnO/TiO\textsubscript{2}/Pt photocathode under similar conditions. We tentatively attribute this to lower photoelectrochemical properties of our bare Cu\textsubscript{2}O electrode compared with the bare electrode employed by Paracchino et al (0.37mA.cm\textsuperscript{-2} compared with 2.5mA at E\textsubscript{appl} of +0.3V vs. RHE). We can therefore expect higher performance of the hybrid photocathode once the photoelectrochemical properties of our bare Cu\textsubscript{2}O are improved.

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References and Notes


