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New Earth-abundant Materials for Large-scale Solar Fuels Generation

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Abstract: The solar resource is immense, but the power density of light striking the Earth’s surface is relatively dilute, necessitating large area solar conversion devices in order to harvest substantial amounts of power for renewable energy applications. In addition, energy storage is a key challenge for intermittent renewable resources such as solar and wind, which adds significant cost to these energies. As the majority of humanity’s present-day energy consumption is based on fuels, an ideal solution is to generate renewable fuels from abundant resources such as sunlight and water. In this account, we detail our recent work towards generating highly efficient and stable Earth-abundant semiconductor materials for solar water splitting to generate renewable hydrogen fuel.

Keywords: Copper oxide · Hydrogen · Photoelectrochemical water splitting · Sb$_2$Se$_3$ · Solar fuels

1. Introduction and Motivation

I started my undergraduate studies at the University of Georgia in 1998. I had many times participated in a Musical Theatre Camp in my hometown of Cartersville, Georgia, and so I began my studies as a Drama major, thinking I might be a Broadway actor. After one rather uninteresting semester, I quickly decided that this would perhaps be a better hobby than a career. My next idea was to be a medical doctor, and so I was therefore taking the required science curriculum. I had to take the dreaded organic chemistry course, but I found that I actually really liked it. I was attracted to the creativity of synthesis, with finding the most efficient routes to synthesis target molecules. I moved to Berkeley in 2002 to begin my PhD in the field of chemical biology, which was gaining in popularity at the time. I was part of the group effort to develop site-selective protein modification reactions for new biomaterials, and I pioneered a new method to selectively target the tyrosine residues of proteins using palladium π-allyl complexes. Towards the end of my PhD, I felt drawn towards more focused synthetic chemistry, and joined the laboratory of Prof. Erik Sorensen at Princeton University as a post-doctoral researcher to further develop my synthetic skills, pursuing a total synthesis of hirsutellone B. As I prepared to apply for faculty positions, I wrote proposals that used my skill set in organic synthesis and chemical biology and applied it towards a new and intriguing field: solar energy conversion to fuels. After consulting with my advisors, I decided that another post-doctoral position would be beneficial to really get into such a completely new field, and I applied to the International Research Fellowship Program of the National Science Foundation (USA), where I was awarded a fellowship that allowed me to learn semiconductor-based water splitting in the renowned laboratory of Prof. Michael Graetzel. There, I directed my efforts towards the synthesis of new inorganic materials for solar water splitting to generate hydrogen fuel.

In this account, we highlight a few of the recent results from our laboratory that focus on efficient and stable Earth-abundant semiconductor materials, with an eye towards large-scale water splitting.

2. Antimony Selenide (Sb$_2$Se$_3$)

Antimony selenide is an ‘emerging material’ for thin film solar cell applications, with efficiencies as high as 6.5% reported in the literature. With a band gap similar to silicon (~1.2 eV), it is ideal for coupling with a wide band gap photoanode to fabricate a tandem photoelectrochemical cell for unassisted water-splitting applications. With very few reports in the literature for water splitting, p-type Sb$_2$Se$_3$ was a promising candidate for investigation as a photocathode for H$_2$ evolution. Sb$_2$Se$_3$ thin films were fabricated in a very simple fashion, by seleniumization of electrodeposited Sb metal with elemental selenium at 350 °C for 40 minutes in a tube furnace. The Sb$_2$Se$_3$ thin films obtained were indexed with the orthorhombic phase of Sb$_2$Se$_3$, with no signs of secondary phases or impurities from the X-ray diffraction patterns. In order to be employed as a photocathode for water splitting applications, the conduction band edge position must lie above the thermodynamic potential for H$_2$ evolution (0 V vs RHE). The conduction band position was estimated through a combination of Mott-Schottky analysis and X-ray photoelectron spectroscopy (XPS) to be approximately...
-0.4 V vs RHE, and therefore suitable for use as a photocathode for $\text{H}_2$ evolution. Fig. 1a shows the device architecture of the $\text{Sb}_2\text{Se}_3$ photocathode where an Earth-abundant catalyst ($\text{MoS}_2$) is employed for $\text{H}_2$ evolution in 1 M $\text{H}_2\text{SO}_4$ electrolyte solution under simulated one sun illumination (AM 1.5 G, 100 mW cm$^{-2}$). The bare $\text{Sb}_2\text{Se}_3$ without the $\text{MoS}_2$ catalyst showed negligible photocurrent, whereas the $\text{MoS}_2$ catalyst-coated $\text{Sb}_2\text{Se}_3$ showed photocurrent density as high as 5.2 mA cm$^{-2}$ at 0 V vs RHE. Gas chromatography measurements confirmed that the large amount of bubbles produced during operation were in fact $\text{H}_2$, with $\sim$100% faradaic efficiency. To improve the photocurrent onset of the $\text{Sb}_2\text{Se}_3$, a post-sulfurization treatment was performed. This treatment resulted in the formation of a thin antimony sulfide ($\text{Sb}_2\text{S}_3$) layer, which has an ionization potential higher than the $\text{Sb}_2\text{Se}_3$, leading to a valence band offset at the $\text{Sb}_2\text{S}_3$/Sb$_2$Se$_3$ interface. Such an offset should act as a hole blocking layer, which could result in reduced surface recombination. This was reflected in the photoelectrochemical (PEC) performance of a sulfurized photocathode ($\text{Sb}_2\text{Se}_3$-$\text{MoS}_2$-$\text{S}$), which exhibited an improved photocurrent onset ($\sim$100 mV earlier) and high photocurrent densities ($\sim$14 mA cm$^{-2}$) at 0 V vs RHE (Fig. 1b). This improvement was also evident from the incident photon conversion efficiency (IPCE) spectrum, where the sulfurized sample showed high IPCE values across the entire absorption spectrum of $\text{Sb}_2\text{Se}_3$.

It is also noteworthy that the band gap was unaffected by the sulfurization treatment, and STEM-EDX mapping showed that there was no sulfur penetration deep into the $\text{Sb}_2\text{Se}_3$ film (Fig. 2a). Upon investigating the surface of the sulfurized and non-sulfurized samples by XPS, the $\text{Sb}_2\text{O}_3$ content decreased after the sulfurization treatment. This oxide layer was partially converted to $\text{Sb}_2\text{S}_3$ (confirmed by Raman spectroscopy), which we hypothesize acts as a hole blocking layer at the $\text{Sb}_2\text{Se}_3$ surface, resulting in an improvement of PEC performance (Fig. 2b and 2c).

$\text{Sb}_2\text{Se}_3$-$\text{MoS}_2$ ($\text{sulfurized}$) exhibited a 30% degradation of photocurrent in the strongly acidic conditions (pH 0) after 2 h at 0 V vs RHE under illumination. However, upon re-application of $\text{MoS}_2$ catalyst, the photocurrent density was restored to nearly the initial value. This observation points to a loss of $\text{MoS}_2$ catalyst during operation, which was also confirmed by XPS measurements of both freshly prepared and measured samples that show loss of Mo and S signal after operation. With a thicker coating of $\text{MoS}_2$ (~30 nm), better photocurrent stabilities were obtained for the non-sulfurized samples (up to 20 h in 1 M $\text{H}_2\text{SO}_4$ at 0 V vs RHE) (Fig. 3a). However, the high-performing sulfurized sample slowly degraded to nearly 0 mA cm$^{-2}$ after 20 h. To identify the origin of this performance loss, a dark electrolysis experiment of $\text{MoS}_2$ on glassy carbon electrode was performed, which showed that the $\text{MoS}_2$ catalyst slowly degraded to nearly 0 mA cm$^{-2}$ after 20 h, again pointing to a problem of the catalyst. In this case, the degradation of the $\text{MoS}_2$ catalyst could be attributed to conversion of the $\text{MoS}_2$ to $\text{MoO}_3$, which results in reduced catalytic activity of the catalyst. The XPS spectra before and after showed a large increase in the oxygen content of the $\text{MoS}_2$ catalyst surface after 20 h operation. These investigations suggest that the instability of the $\text{Sb}_2\text{Se}_3$-$\text{MoS}_2$-$\text{S}$ photocathode is primarily due to the $\text{MoS}_2$ catalyst and not to the $\text{Sb}_2\text{Se}_3$. To confirm the intrinsic stability of the $\text{Sb}_2\text{Se}_3$ thin film, a photocorrosion stress test was performed where the bare $\text{Sb}_2\text{Se}_3$ film was subjected to 285 cyclic voltamgrams in 1 M $\text{H}_2\text{SO}_4$ under one sun illumination during a 4.75 h experiment (Fig. 3b). After this stress test $\text{MoS}_2$ catalyst was deposited, and the sample exhibited similar PEC performance to the typically prepared $\text{Sb}_2\text{Se}_3$-$\text{MoS}_2$ samples. This important finding shows that $\text{Sb}_2\text{Se}_3$ is intrinsically stable to photocorrosion in strong acid (in contrast to other high efficiency photocathodes), and is therefore a strong candidate for practical, large-scale PEC water splitting.

3. Copper Oxides

An alternative strategy to finding materials that are intrinsically stable in the harsh
that the dark current was significantly reduced upon deposition of the TiO\textsubscript{2} overlayer, due to prevention of the photocorrosion of the CuO layer. The protection strategy enabled a stable photocurrent density over a period of 1 h at 0 V vs RHE under one sun illumination, and the photocurrent obtained was confirmed to be H\textsubscript{2} evolution from gas chromatography experiments. In order to gain a better understanding of the electrical properties of the CuO absorber, Mott-Schottky analysis was performed and the carrier density was estimated. The acceptor density was found to be very high, on the order of 10\textsuperscript{17} cm\textsuperscript{-3}, which can be attributed to a large number of copper vacancies. The high doping results in a very narrow space-charge region, which limits the charge collection efficiency. This was also reflected in the IPCE spectrum of the CuO photocathode where the low energy photons (> 650 nm) absorbed deeper in the film were not able to be extracted due to the short diffusion length of the photogenerated electrons. Therefore, optimization of the CuO synthesis or doping could help reduce the acceptor density and hence improve the carrier collection length of CuO photocathodes, which would pave the way for higher PEC performance.

### 3.2 Cuprous Oxide (Cu\textsubscript{2}O)

Cuprous oxide, a p-type semiconductor with a band gap of 2.0 eV, is a promising Earth-abundant material for hydrogen evolution photocathodes. Theoretically, a large photocurrent density of 14.7 mA cm\textsuperscript{-2} can be achieved under one sun illumination.\textsuperscript{[11]} To solve the poor stability issue of Cu\textsubscript{2}O in aqueous media, pioneering work was carried out by the Graetzel group who developed a multilayer composite photocathode consisting of a buried p-n junction (p-Cu\textsubscript{2}O and n-ZnO or n-AZO), a TiO\textsubscript{2} protective layer, and a surface hydrogen evolution catalyst. Photocurrents as high as 7.6 mA cm\textsuperscript{-2} were obtained at 0 V vs RHE, however, the onset potential was still relatively negative (~0.5 V vs RHE).\textsuperscript{[12]} This results from the small photovoltage generated by the buried p-n junction, which usually gives ~0.5 V open circuit voltage (V\textsubscript{oc}) in the corresponding photovoltaic devices.\textsuperscript{[13]} In this view, an ultrathin Ga\textsubscript{2}O\textsubscript{3} layer was applied to replace the ZnO or AZO layer. Due to the more favorable band alignment, a very positive onset potential was observed by Li and co-workers (1.02 V vs RHE) as well as a photocurrent of 2.95 mA cm\textsuperscript{-2} at 0 V vs RHE.\textsuperscript{[14]}

Recently, we fabricated a thermally-oxidized Cu\textsubscript{2}O based photocathode (TO-Cu\textsubscript{2}O),\textsuperscript{[15]} which is schematically illustrated in Fig. 5. After the thermal oxidation of copper foil, Ga\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} layers were subsequently deposited on the front side...
of the foil by the atomic layer deposition (ALD) technique. Next, a thin Au layer was coated on the back side to serve as the back contact, and connected with a Cu wire. After coating with an electrodeposited RuO$_2$ catalyst, this TO-Cu$_2$O photocathode exhibits an onset potential of 0.9 V vs RHE and large photocurrents even at substantially positive potential (e.g. 3.5 mA cm$^{-2}$ at 0.5 V vs RHE) in pH 5 electrolyte.

Previous work in photovoltaics have already shown that TO-Cu$_2$O has a more effective absorption and better conversion of photons from the green and red part of the solar spectrum, compared to the widely used Cu$_2$O by electrodeposition (ED-Cu$_2$O). Therefore, we designed a dual Cu$_2$O photocathode by coupling a front transparent ED-Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/RuO$_2$ photocathode with a back TO-Cu$_2$O/Ga$_2$O$_3$/TiO$_2$/RuO$_2$ photocathode, as shown in Fig. 6. With optimized thicknesses of each Cu$_2$O layer, this dual Cu$_2$O photocathode configuration showed an enhanced photocurrent density of 3.67 mA cm$^{-2}$ at 0.5 V vs RHE, and a new record energy conversion efficiency of 1.9% at +0.45 V vs RHE, as shown in Fig. 7a. The enhanced photocurrents at low applied bias are of great significance for the developing of high efficiency tandem cells. The IPCE curve of this dual photocathode is presented in Fig. 7b, together with those of the individual front ED and back TO-Cu$_2$O photocathodes. The TO-Cu$_2$O photocathode has much stronger conversion near the Cu$_2$O band edge (500–620 nm) than the ED sample, while the ED-Cu$_2$O photocathode shows better use of the blue light (<450 nm), enabling efficient photon conversion over the entire absorption spectrum of Cu$_2$O.

4. Perspective and Outlook

Photoelectrochemical water splitting is a promising route to large-scale renewable hydrogen production. Unlike alternative technologies such as photovoltaic-coupled electrolysis, the integrated PEC approach allows smart thermal management that increases the overall device efficiency, as the electrolyte cools the irradiated photobuffer--enabling a larger output photovoltage--while the increased temperature of the electrolyte improves the efficiency of the photocatalytic fuel generation reaction.$^{[16]}$ However, in order to be cost competitive with photovoltaic-coupled electrolysis, improvements in the efficiency and stability of the PEC cells must be obtained, which is a significant challenge. The strategy of using protective layers to stabilize intrinsically unstable materials enables any photovoltaic material to be used, including highly developed photovoltaic materials such as silicon, which would normally corrode in the harsh electrolyte solution. Although some examples in the literature have demonstrated weeks of stability, it remains uncertain whether this strategy will be suitable for the years of stability that are required. Ideally, new materials will be found that are both highly efficient and intrinsically stable without the need for protective layers. Sb$_3$Se$_5$ is a promising candidate, as it is resistant to photocorrosion in 1 M H$_2$SO$_4$ and gives very high hydrogen-producing photocurrents under strong electrical bias. The photovoltagge of this material must be improved, however, which is a current topic of research in our group.

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