# Efficient Water Splitting on Z-scheme Photocatalyst Sheets using Oxysulfides as Hydrogen Evolution Photocatalysts

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**Abstract:**$La_5Ti_2CuS_5O_7$(LTC) as a hydrogen evolution photocatalyst (HEP)realized water splitting by constructing Z-scheme-type photocatalyst sheets with $BiVO_4$ as the oxygen evolution photocatalyst (OEP). p-type doping and the formation of a $La_5Ti_2Cu_{0.9}Ag_{0.1}S_5O_7$ solid solution effectively enhance the performance of the photocatalyst sheet. An apparent quantum yield (AQY) of 3.2% at 420 nm and a solar-to-hydrogen energy conversion efficiency (STH) of 0.11% were obtained, both of which are among the highest values reported for water splitting systems employing a particulate photocatalyst absorbing visible light up to ca. 700 nm.

**Keywords:** Z-scheme water splitting, photocatalyst sheet, oxysulfides.

## 1. Introduction

(Oxy)sulfides, which exhibit intense visible light absorption and high photocatalytic activities for hydrogen evolution, are promising HEPs for Z-scheme water splitting. Sulfides have been applied to Z-scheme water splitting systems in which electron transfer is mediated by a solid-state electron mediator[1,2]or an aqueous redox mediator[3]. However, existing visible-light-driven Z-scheme systems involving (oxy)sulfide photocatalysts show STH of $3\times10^{-3}$% at most.[4] The main obstacles to further improvements are backward reactions, that is, reduction and oxidation of redox couples on the HEP and OEP, respectively, and inefficient interparticle charge transfer between the HEP and the OEP.

The concept of particulate photocatalyst sheets represents a new approach to addressing the aforementioned challenges associated with conventional Z-scheme systems[5]. Here, we report the application of photocatalyst sheets based on LTC as the HEP and $BiVO_4$ as the OEP to Z-scheme water splitting. The activity of such sheets is shown to be boosted by enhancing the activity of the LTC as a photocathode through p-type doping and the formation of a $La_5Ti_2Cu_{0.9}Ag_{0.1}S_5O_7$(LTCA) solid solution, yielding an AQY of 3.2% at 420 nm and a STH of 0.11 %.

## 2. Experimental

LTC-based oxysulfides were prepared by a solid-state reaction based on our previous studies[6]. $BiVO_4$ powder was synthesized by a solid-liquid reaction[7].The photocatalyst sheets with a Au conductor layer were fabricated using a particle transfer method[5]. The photodeposition of cocatalysts ($Cr_2O_3$/M, M = Rh, Pt, and Ru) was carried out under visible light irradiation ($\lambda$> 420 nm) from a Xe lamp using a closed circulation system. Water splitting reactions over the photocatalyst sheets were carried out using a Pyrex top-irradiation reactor connected to a glass closed gas circulation system. In each trial, a photocatalyst sheet sample ($3 \times 3$ $cm^2$, effective area: ~8 $cm^2$) was placed at the bottom of the reactor, which held 40 mL of distilled water.

## 3. Results and discussion

LTC/Au/$BiVO_4$ sheet without a cocatalyst did not evolve $H_2$ or $O_2$under visible light irradiation because of the lack of $H_2$ evolution sites on the LTC. Sheets were therefore loaded with noble metal cocatalysts followed by the addition of $Cr_2O_3$ by photodeposition. $Cr_2O_3$ was deposited to inhibit the formation of water from the $H_2$ and $O_2$reaction products as well as to limit the oxygen reduction reaction on the noble metal cocatalysts. As shown in Figure 1, after the loading of the $Cr_2O_3$/Rh cocatalysts, the LTC/Au/$BiVO_4$ sheets evolved $H_2$ and $O_2$ at the expected stoichiometric molar ratio of two. Notably, the activity of the sheets was greatly enhanced following doping with lower valence cations such as $Ga^{3+}$, $Al^{3+}$, $Sc^{3+}$, and $Mg^{2+}$ at the Ti-sites of the LTC and forming LTCA solid solutions. Therein, a $Cr_2O_3$/Rh/Ga-LTCA/Au/$BiVO_4$ sheet evolved $H_2$ and $O_2$of 20.2 μmolh$^{-1}$ and 10.1 μmol h$^{-1}$, respectively. The results indicated that the activity of the present sheet system was strongly correlated with the activity of the HEP as a photocathode rather than as a powder suspension.

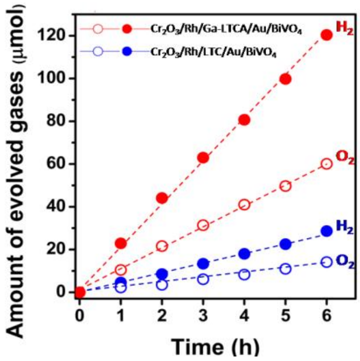

**Figure 1.**Time courses of overall water splitting over a $Cr_2O_3$/Rh/LTC/Au/$BiVO_4$ sheet and $Cr_2O_3$/Rh/Ga-LTCA/Au/$BiVO_4$ sheet.

An AQY of 3.2% at 420 nm was obtained from a $Cr_2O_3$/Rh/Ga-LTCA/Au/$BiVO_4$ sheet (Figure 2). The STH value of 0.11% obtained in these trials is two orders of magnitude greater than that was observed in our previous work with oxysulfide-based Z-scheme systems using an aqueous $I_3^-/I^-$ redox mediator. Both AQY and STH values are the highest yet reported for a Z-scheme system involving a particulate photocatalyst absorbing light up to ca. 700 nm.

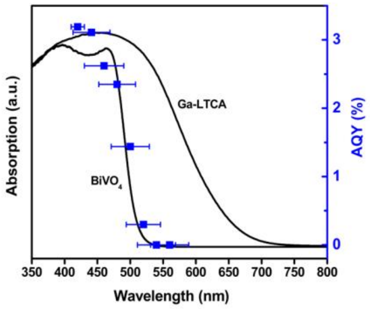

**Figure2.** AQY of a $Cr_2O_3$/Rh/Ga-LTCA/Au/$BiVO_4$ sheet as a function of the incident light wavelength.

## 4. Conclusions

Water splitting without a redox couple was achieved by applying LTC as the HEP and$BiVO_4$as the OEP to construct Z-scheme-type sheets. An AQY of 3.2% at 420 nm and a STH of 0.11% were obtained when using Ga-LTCA as the HEP. We believe that this visible-light-driven water splitting system could be further enhanced through replacing $BiVO_4$ with an OEP having a narrower band-gap so as to fully take advantage of the ability of the Ga-LTCA to remain active up to 710 nm.

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