Photocatalytic water splitting promoted by Al-doped SrTiO\textsubscript{3} coloaded with molybdenum oxide and rhodium-chromium oxide

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Abstract: The study was investigated enhancing the water splitting activity of highly efficient cocatalyst/photocatalyst composites by coloading a small amount of molybdenum oxide (MoO\textsubscript{x}), followed by calcination. Reductively photodeposited MoO\textsubscript{3} modifies the chemical state of the RhCrO\textsubscript{3} cocatalyst and likely promotes photocatalytic H\textsubscript{2} evolution, whereas MoO\textsubscript{3} loaded onto STO:CrO\textsubscript{2} catalyzes neither photocatalytic H\textsubscript{2} nor O\textsubscript{2} evolution. Al-doped SrTiO\textsubscript{3} loaded with a MoO\textsubscript{3} and rhodium-chromium mixed oxide (MoO\textsubscript{3}/RhCrO\textsubscript{3}/STO:Al) has the highest apparent quantum yield (AQY) of 69% under 365 nm ultraviolet (UV) light.

Keywords: photocatalyst, cocatalyst, water splitting.

1. Introduction

Molybdenum oxides have recently been demonstrated to function as electrocatalysts for hydrogen evolution [1, 2]. Some molybdenum oxides have also been applied as cocatalysts for photocatalytic water splitting. Busser et al. [3] studied CuO/\textsubscript{2}CrO\textsubscript{3}/MoO\textsubscript{3}-modified Ga\textsubscript{2}O\textsubscript{3} photocatalysts meant for overall water splitting and reported that these materials showed excellent activity and stability. The application of a Mo coating on a Pt/SrTiO\textsubscript{3} photocatalyst was shown to suppress the backward reactions on Pt in a similar manner to a Cr\textsubscript{2}O\textsubscript{3} coating [4]. Therefore, the loading of molybdenum oxides is also expected to enhance the water splitting activity of various photocatalysts. In the present work, the coloading of MoO\textsubscript{3} cocatalysts onto RhCrO\textsubscript{3}/STO:Al photocatalysts was studied in an attempt to improve the activity of the original materials. It was found that coloading MoO\textsubscript{3} by photodeposition and calcination did indeed enhance the water splitting activity of these photocatalysts, such that the AQY was improved by 20%, to 69%, at 365 nm. The characteristics and photocatalytic water splitting activities of these MoO\textsubscript{3} and RhCrO\textsubscript{3}-coloaded STO:Al photocatalysts are discussed herein.

2. Experimental

MoO\textsubscript{3} was loaded onto the RhCrO\textsubscript{3}/STO:Al by photodeposition. The RhCrO\textsubscript{3}/STO:Al photocatalyst (0.20 g) was dispersed in distilled water (100 mL) containing varying amounts of Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O (Sigma-Aldrich Co, LLC) as the Mo precursor. The MoO\textsubscript{3} loading was determined by the amount of Mo added to the solution (0–10 wt% with respect to the RhCrO\textsubscript{3}/STO:Al powder). Photodeposition was carried out using a closed gas-circulation system. The suspension was contained in a top-irradiation reactor and evacuated to completely remove air, after which it was irradiated using a 300 W xenon lamp (300 nm < λ < 500 nm), equipped with a dichroic mirror, through a Pyrex window for 4 h. The powder was subsequently collected and dried in an oven at 313 K, following which the MoO\textsubscript{3}/RhCrO\textsubscript{3}/STO:Al was calcined at 573 K in air for 1 h. In some cases, the calcination temperature was varied within the range from 313 K (that is, no calcination) to 673 K.

3. Results and discussion

Figure 1 shows the water splitting rates obtained from MoO\textsubscript{3}/RhCrO\textsubscript{3}/STO:Al samples having different Mo loadings and calcined at 573 K under UV irradiation. The H\textsubscript{2} and O\textsubscript{2} evolution rates were increased with increases in the Mo loading from 0 to 5 wt%. However, excessive loading of MoO\textsubscript{3} (more than 8 wt% Mo)
lowered the gas evolution rates, presumably because the MoO\textsubscript{y} blocked surface active sites on the RhCrO\textsubscript{x}/STO:Al photocatalyst and also shaded the photocatalyst. The loading of an excess of a cocatalyst generally decreases the activity of photocatalysts [5]. In addition, Figure 1(b) presents the water splitting rates obtained from MoO\textsubscript{y}/RhCrO\textsubscript{x}/STO:Al photocatalysts (Mo 5 wt\%) calcined at different temperatures for 1 h. The gas evolution rates evidently increased with the calcination temperature up to 573 K. However, the sample calcined at 673 K showed almost the same activity as that of the pristine RhCrO\textsubscript{x}/STO:Al and thus was not improved by the coloading of MoO\textsubscript{y}. This result can most likely be attributed to the aggregation of the RhCrO\textsubscript{x} cocatalyst during calcination at 673 K [28]. Consequently, the MoO\textsubscript{y}/RhCrO\textsubscript{x}/STO:Al calcined at 573 K exhibited the highest water splitting activity, with an AQY of 69 ± 1.4\% at 365 nm.

Figure 1. (a) The photocatalytic activity of MoO\textsubscript{y}/RhCrO\textsubscript{x}/STO:Al under UV irradiation (300 nm < \lambda < 500 nm) as a function of the amount of Mo added. All samples were calcined at 573 K. (b) Dependence of the photocatalytic activity of MoO\textsubscript{y}/RhCrO\textsubscript{x}/STO:Al under UV irradiation (300 nm < \lambda < 500 nm) on the different calcination temperature. The MoO\textsubscript{y} loading of each sample was 5 wt\% as Mo.

4. Conclusions

This study demonstrated that the water splitting activity of highly-active RhCrO\textsubscript{x}/STO:Al photocatalysts can be enhanced by loading a relatively low amount (5 wt\%) of Mo species. Calcination of the MoO\textsubscript{y}/RhCrO\textsubscript{x}/STO:Al photocatalyst at 573 K further improved their water splitting activity. The resulting AQY of 69\% at 365 nm is the highest yet reported for overall water splitting in this wavelength region.

References