Photocatalytic water splitting promoted by Al-doped $SrTiO_3$ 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_y), followed by calcination. Reductively photodeposited MoO_y modifies the chemical state of the $RhCrO_x$ cocatalyst and likely promotes photocatalytic H_2 evolution, whereas MoO_y loaded onto STO:Al catalyzes neither photocatalytic H_2 nor O_2 evolution. Al-doped $SrTiO_3$ loaded with a MoO_y and rhodium-chromium mixed oxide (MoO_y /$RhCrO_x$/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 $CuO_z/CrO_y/MoO_x$-modified Ga_2O_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/$SrTiO_3$ photocatalyst was shown to suppress the backward reactions on Pt in a similar manner to a Cr_2O_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_y cocatalysts onto $RhCrO_x$/STO:Al photocatalysts was studied in an attempt to improve the activity of the original materials. It was found that coloading MoO_y 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_y and $RhCrO_x$-coloaded STO:Al photocatalysts are discussed herein.

2. Experimental

MoO_y was loaded onto the $RhCrO_x$/STO:Al by photodeposition. The $RhCrO_x$/STO:Al photocatalyst (0.20 g) was dispersed in distilled water (100 mL) containing varying amounts of $Na_2MoO_4 \cdot 2H_2O$ (Sigma-Aldrich Co, LLC.) as the Mo precursor. The MoO_y loading was determined by the amount of Mo added to the solution (0–10 wt% with respect to the $RhCrO_x$/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 ($300 \text{ nm} < \lambda < 500 \text{ nm}$), 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_y/$RhCrO_x$/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_y/$RhCrO_x$/STO:Al samples having different Mo loadings and calcined at 573 K under UV irradiation. The H_2 and O_2 evolution rates were increased with increases in the Mo loading from 0 to 5 wt%. However, excessive loading of MoO_y (more than 8 wt% Mo) lowered the gas evolution rates, presumably because the MoO_y blocked surface active sites on the $RhCrO_x$/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_y/$RhCrO_x$/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 $RhCrO_x$/STO:Al and thus was not improved by the coloading of MoO_y. This result can most likely be attributed to the aggregation of the $RhCrO_x$ cocatalyst during calcination at 673 K [28]. Consequently, the MoO_y/$RhCrO_x$/STO:Al calcined at 573 K exhibited the highest water splitting activity, with an AQY of 69 ± 1.4% at 365 nm.

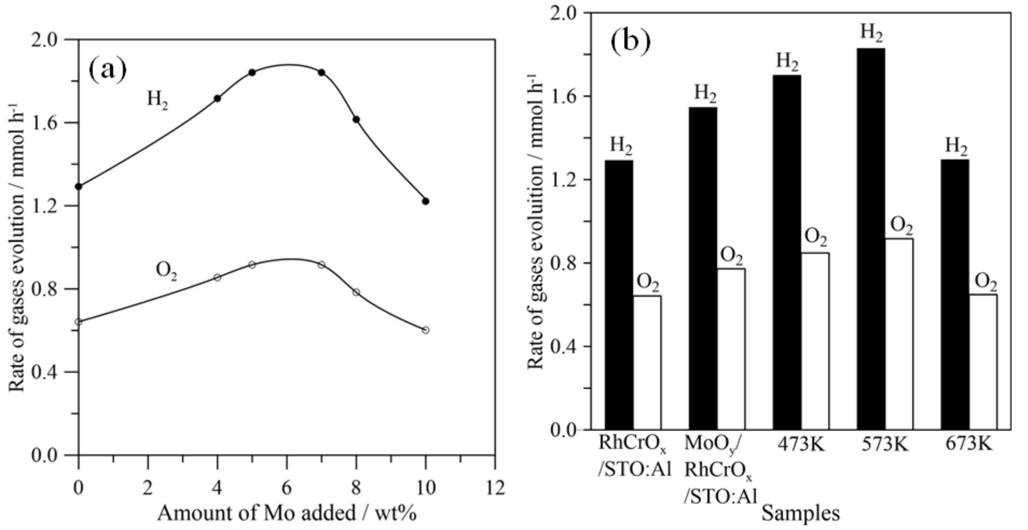

Figure 1. (a) The photocatalytic activity of MoO_y/$RhCrO_x$/STO:Al under UV irradiation (300 nm < λ < 500 nm) as a function of the amount of Mo added. All samples were calcined at 573 K. (b) Dependence of the photocatalytic activity of MoO_y/$RhCrO_x$/STO:Al under UV irradiation (300 nm < λ < 500 nm) on the different calcination temperature. The MoO_y loading of each sample was 5 wt% as Mo.

4. Conclusions

This study demonstrated that the water splitting activity of highly-active $RhCrO_x$/STO:Al photocatalysts can be enhanced by loading a relatively low amount (5 wt%) of Mo species. Calcination of the MoO_y/$RhCrO_x$/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

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