

# Low-Cost Roll-Press Fabricated Particulate Photocatalyst Sheets Based on Metal Substrates for Large-Area Pure-Water Splitting Under Visible Light

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**Abstract:** Particulate photocatalyst sheet is a simple and environmentally friendly photocatalyst type for water splitting in heterogeneous catalytic system. However, large-scale photocatalyst sheets fabrication is yet to be demonstrated. This study has focused on the development of a scalable roll-press method to fabricate particulate photocatalyst sheets based on metal substrates. We systematically studied the hydrogen generation rate of photocatalyst sheets as a function of metal substrate species, calcination temperature, and time. To date, the roll-press method prepared SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Ti sheet showed stably H<sub>2</sub> generation and exhibited an solar-to-hydrogen energy conversion efficiency of ~ 0.29%.

**Keywords:** hydrogen production, Scalability, Roll-press.

## 1. Introduction

Water splitting on semiconductors has long been studied as a potential approach for converting solar energy into renewable hydrogen. Z-scheme water splitting system, combining two different semiconductors using a shuttle redox mediator, is one of the possible forms of artificial photocatalytic water splitting. Particulate photocatalyst sheet, a type of Z-scheme system using solid-state mediator (metals or carbon sheet) as the shuttle redox mediator, is a simple and environmentally friendly catalyst type in heterogeneous catalytic system without further wastewater treatment. Particle transfer method and screen printing method are two of the main methods to preparation of photocatalyst sheets. However, considerably high vacuum, extra organic or noble metals additives are required using those methods. In this study, we focused on the development of a scalable and simple roll-press method to fabricate photocatalyst sheets based on metal substrates. We systematically studied the hydrogen generation rate of SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Metal sheets as a function of metal substrate species, calcination temperature, and time.

## 2. Experimental

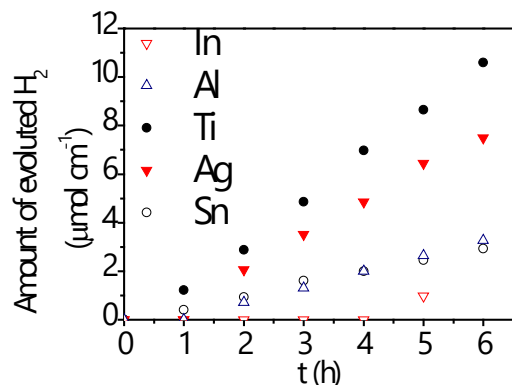
SrTiO<sub>3</sub>:La,Rh and BiVO<sub>4</sub>:Mo were synthesized according to previously reported procedures.<sup>1,2</sup> SrTiO<sub>3</sub>:La,Rh /BiVO<sub>4</sub>:Mo/Metal photocatalyst sheets were fabricated by the roll-press method. A mixture of SrTiO<sub>3</sub>:La,Rh and BiVO<sub>4</sub>:Mo powders was dispersed in of isopropanol by sonication. The suspension was then drop-cast on a metal substrate (In, Al, Sn, Ag, or Ti). The photocatalyst coated metal substrate was dried at room temperature before roll-pressing. In the roll-press, two cylindrical rollers rotated on one another at a desired pressure. Finally, the sheet was placed into a furnace, followed by heating at 10 K min<sup>-1</sup> and then holding at the respective temperature for 20-40 min.

Prior to the overall water splitting reaction, the photocatalyst sheet samples were modified with cocatalyst.<sup>3</sup> Water-splitting reactions were also performed in the same closed gas circulation system with top irradiation by a 300 W Xe lamp equipped with a cutoff filter ( $\lambda > 420$  nm). The photocatalyst sheet samples (ca. 4 cm<sup>2</sup>) were placed at the bottom of the reaction cell containing 100 mL pure water without any additives. The reaction temperature and the background pressure were 288 K and 5 kPa, respectively.

## 3. Results and discussion

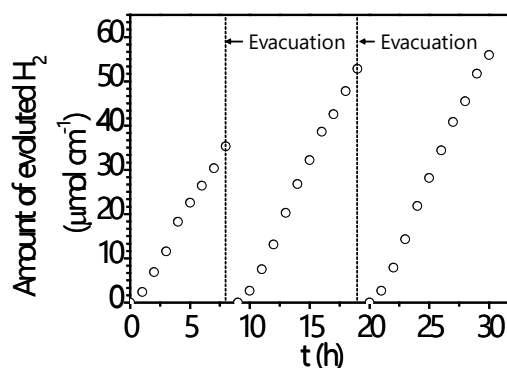
Theoretically, the hardness and the work function of metal substrates can influence the contact and electron-hole separation between the semiconductors and the metal substrates. We first examined the effect

of metal substrate species in order to find the best metal substrate for the fabrication of photocatalyst sheets using roll-press method. Metals, In, Al, Ti, Ag, and Sn were employed as the substrate for SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Metal sheets fabrication, irrespectively.



**Figure 1.** Time courses of the H<sub>2</sub> evolution during water splitting reaction on Ru-modified SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Metal photocatalyst sheets. All samples were tested without annealing.

Figure 1 shows the effect of metal substrate species on photocatalytic water splitting rate of Ru-modified SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/metal photocatalyst sheets. Titanium substrate shows the highest H<sub>2</sub> generation rate compared with other metal substrates. Therefore, we further explore the optimal fabrication conditions for SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Metal sheets based on Ti metal substrate in terms of calcination temperature and time and tested their water splitting ability under visible light illumination. The optimum condition of SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Ti sheets for water splitting is calcination at 400 °C for 30 min.



**Figure 2.** Time course of H<sub>2</sub> evolution during Z-scheme water splitting using Ru-modified SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Ti photocatalyst sheets. Photocatalyst sheets fabrication conditions: calcination temperature, 400 °C; calcination time, 30 min.

Figure 2 shows the time course of H<sub>2</sub> evolution during Z-scheme water splitting using Ru-modified SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Ti photocatalyst sheets which prepared under the optimum condition. H<sub>2</sub> generated stably during the tested 30 h and the solar-to-hydrogen energy conversion efficiency (STH) is ~ 0.29% for water splitting.

#### 4. Conclusions

The fabrication of SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo/Metal photocatalyst sheets using simple roll-press method was systematically studied. Among various metal substrates (In, Al, Sn, Ag, or Ti), Ti was found to be the most suitable metal for the SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo Z-scheme water splitting system due to the appropriate work function and hardness. To date, the Ti metal based SrTiO<sub>3</sub>:La,Rh/BiVO<sub>4</sub>:Mo photocatalyst sheet generated H<sub>2</sub> stably and exhibited an STH of ~ 0.29%. Roll-press method is a simple and scalable method to fabricate efficient photocatalyst sheets for water splitting and further studies are in progress.

#### References

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