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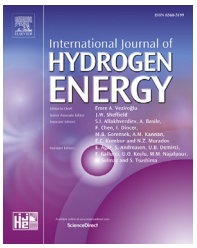

# Kilogram-scale production of highly active chalcogenide photocatalyst for solar hydrogen generation

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ABSTRACT

Solar photocatalytic hydrogen production from water has been regarded as an ideal way addressing world energy and environmental crises. The technology has long relied on the development of an efficient photocatalyst. In addition to its photocatalytic performance, the large-scale production of certain photocatalyst from the viewpoint of particle application remains a challenge yet has received insufficient focus. Herein, we report an efficient and practical batch preparation system based upon hydrothermal method to the scalable production of chalcogenide nanoparticle photocatalyst. Taking the synthesis of $Cd_{0.5}Zn_{0.5}S$ (CZS) twinned photocatalyst as an example, the outcome of CZS photocatalyst could reach ~0.8 kg in this batched synthesis, which is about 390 times of the lab-scale production in mass amount. It was found that the twinned structure and visible-light absorption property were well maintained. Although further measurements toward the photocatalytic activity indicate slight decrement on solar $H_2$ generation compared to the lab-scale synthesized CZS photocatalyst, a high quantum efficiency of about 40.5% at 425 nm remained. The photocatalytic reaction could also stably proceed for 200 h without notable decay of $H_2$-evolution rate. This work thus provides a powerful means for facile scaling up the chalcogenide nanoparticle photocatalyst at the kilogram level with both high quality and good reproducibility.



## Introduction

Hydrogen has been well-accepted as a future clean energy carrier to address world-wide energy and environmental crises. However, production of hydrogen from renewable resources instead of fossil fuels remains a technological challenge to date. Since the discovery of Honda–Fujishima effect in 1972, in which, water can be photo-split by semiconductor-assisted photocatalysis [1], this technology has received increasing interests as it provides an alternative pathway to the large-scale production of hydrogen [2–6]. The last decade has witnessed a great success in syntheses of semiconductor catalysts with high photocatalytic performance [7–12]. However, this research field remains at the level of academic study. In this case, little attention has paid

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to the large-scale production of photocatalyst particles, which is of great importance to move the study to industrial applications [13,14]. To this end, design and development of batch reactors for scaling up a synthesis of semiconductor photocatalyst is highly desired. Generally, semiconductors photocatalyst can be synthesized *via* hydrothermal, solvothermal, impregnation, coprecipitation, and calcine methods, *etc.* [15–21] Among them, hydro/solvothermal method enables fine-control of nanocrystals in terms of high crystallinity, dispersity, and activity, which make the method a good choice for a scaling-up synthesis [22,23].

To date, there are a few approaches to scale up the production of photocatalyst nanocrystals [24–27]. For example, as shown in Fig. 1, one can amplify a synthesis by using microreactors with continuous flow of droplets [28–30], or just by simply increasing the volume of reaction solution by switching it to larger reactors [31]. These approaches have led to some success with a mass product of nanocrystals up to gram scale. However, the quantity and quality of these syntheses are still far from adequate for the application of industry. Continuous flow of droplets could guarantee the high quality of nanocrystals. But the strict technical requirements as well as limited kinds of products have restricted further extension of the method to synthesis various semiconductor photocatalysts [32]. On the other hand, while the nucleation and growth of colloidal nanocrystals are highly sensitive to experimental conditions such as the way a reagent introduced and mixed, stirring rate, heat management, and variation of temperature [33], it is impossible to expect the same synthesis by just increasing the volume of reaction solution in a larger reactor. Despite the limited success in these large-scale synthesis of the nanocrystals, it is undeniable that the simple technical characteristics of a larger reactor make it deserve to be further investigated for industrial catalyst production.

Herein, we report an attempt to the kilogram-scale production of chalcogenide photocatalyst based upon hydrothermal method by using an amplified reactor. The reactor with a volume of 13 L and equipped with necessary accessories for feedstock, reaction, edulcoration, and purification, has been carefully designed to suit given reactions. By preparing $Cd_{0.5}Zn_{0.5}S$ (CZS) twinned photocatalysts and studying their photocatalytic activity, the reproducibility and reliability of the batched reaction system were demonstrated.

## Experimental section

### *Chemicals and materials*

The chemicals including octan zinecnaty ($ZnAc_2 \cdot 2H_2O$), cadmium dihydrate acetate ($CdAc_2 \cdot 2H_2O$), sodium hydroxide (NaOH), and thioacetamide (TAA) were used as received from Sigma-Aldrich at analytical grade. All aqueous solutions were prepared using de-ionized water with a resistivity of 18.2 MΩ·cm.

### *Lab-scale synthesis of CZS twinned nanocrystals*

Typically, CZS twinned nanocrystals were prepared by a hydrothermal method reported previously [34]. Specifically, $ZnAc_2 \cdot 2H_2O$ (10 mmol) and $CdAc_2 \cdot 2H_2O$ (10 mmol) were dissolved in 40 mL water. NaOH aqueous solution (4 M, 20 mL) was then injected to the solution. A mixture containing $Cd(OH)_2$ and $Zn(OH)_2$ was subsequently formed. TAA (25 mmol) powder was finally introduced into the suspension. Additional water was added to the reaction suspension to maintain a total volume of 80 mL. The entire process was carried out under magnetic stirring. After an extended 20-min stirring, the reaction mixture was transferred to a 100-mL capacity Teflon-lined stainless-steel autoclave. Upon sealing, the reaction mixture was heated to 180 °C in a furnace, and kept at this temperature for 24 h. After cooling, the product was separated by centrifugation, washed with deionized water and ethanol several times, and collected by drying it at

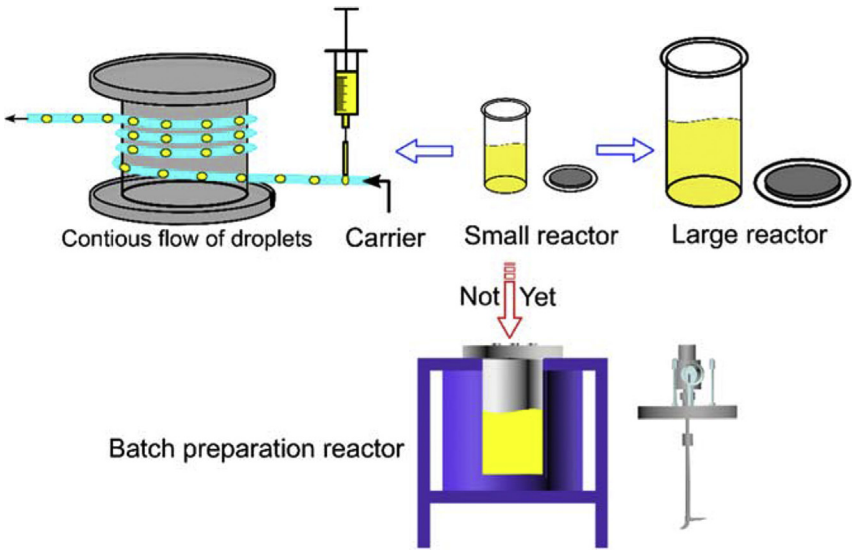


**Fig. 1 – A schematic illustration of two opposite approaches to scale up the production of nanocrystals by either decreasing or increasing in the volume of reaction solution (up). Another approach to scale up the production is to use a larger-volume batch preparation reactor (down).**

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