

# Application of content optimized ZnS-ZnO-CuS-CdS heterostructured photocatalyst for solar water splitting and organic dye decomposition

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**Abstract**—Heterostructured ZnS-ZnO-CuS-CdS photocatalyst was synthesized via a sequential fabrication approach (ZnS→thermal treatment (ZnS-ZnO)→CuS formation (ZnS-ZnO-CuS)→CdS addition (ZnS-ZnO-CuS-CdS)). Each component in this heterostructure has its own role for photocatalytic reaction. The oxide content controlled by thermal processing condition is a crucial factor for improving photocatalytic activity, and the CuS and CdS contents are controlled by their feedstocks. The effects of heterostructure composition on the solar water splitting and organic dye decomposition were investigated under 1 sun irradiation (100 mW/cm<sup>2</sup>, AM 1.5 G filter). The content optimized ZnS-ZnO-CuS-CdS photocatalyst produces 2452.7 μmol g<sup>-1</sup> h<sup>-1</sup> hydrogen, and it decomposes methyl blue much faster than the other cases. Thus, heterostructured photocatalysts can benefit the use of electrons and holes for improved photocatalytic activity.

Keywords: Photocatalytic Hydrogen Production, Dye Decomposition, Heterostructure, ZnS-ZnO-CuS-CdS, Optimal Composition

## INTRODUCTION

Semiconductor materials can absorb photons from light irradiation, and then photoexcited electrons and holes are generated. These electron-hole pairs can react with other substances using oxidation-reduction reactions such as hydrogen production (water splitting), organic dye decomposition, and VOC elimination. These photocatalytic reactions are clean and sustainable; therefore, various researches have been conducted to improve their activities. Major issues in this field are 1) expanding the light absorption range, and 2) improving utilization of electron-hole pairs generated by solar irradiation. There are two promising approaches for improving both light absorption and utilization of electron-hole pairs. The first is to develop new materials such as doped compounds to improve visible light absorption and electron/hole mobility, as reported other studies (Cd<sub>1-x</sub>Zn<sub>x</sub>S [1,2] and Zn<sub>1-x</sub>Cu<sub>x</sub> [3]). The second is to use heterostructure having multi-components playing separate roles for absorbing photons and consuming electron-hole pairs, for example, TiO<sub>2</sub>-CdS [4,5], and ZnS-CuS-CdS [6]. Heterostructured photocatalyst materials have various advantageous characteristics [7] in visible light absorption, fast charge separation, effective cocatalyst and stability from each component. Therefore, a proper combination of components is very important to establish an effective junction (band positions, and electrolyte conditions) in composite structures.

We previously reported the photocatalytic activity of ZnS-CuS-CdS composite on hydrogen production, and it was significantly increased from 13.5 μmol g<sup>-1</sup> h<sup>-1</sup> (pristine ZnS) to 837.6 μmol g<sup>-1</sup>

h<sup>-1</sup> (ZnS-CuS-CdS) [6]. For fabrication of the final composite structure, the pristine ZnS was thermally treated for improved crystallinity before connecting ZnS to CuS and CdS. During the thermal process, the ZnO is naturally formed on ZnS surface, and thus the optimized oxide content in the ZnS-ZnO structure was further examined from various thermal processing temperatures and O<sub>2</sub> partial pressures [8]. From the ZnO formation, the hydrogen production rate was also increased from 13.5 μmol g<sup>-1</sup> h<sup>-1</sup> (pristine ZnS) to 494.8 μmol g<sup>-1</sup> h<sup>-1</sup> (oxide content optimized ZnS-ZnO). Therefore, it is necessary to include the effect of ZnO formation on the photocatalytic activities for the ZnS-ZnO-CuS-CdS heterostructure. Thus, in this study the oxide content was optimized for the ZnS-ZnO-CuS-CdS photocatalyst with its photocatalytic activities by organic dye (methyl blue) decomposition as well as hydrogen production from solar water splitting. To the best of our knowledge, oxide content optimized ZnS-ZnO-CuS-CdS photocatalyst in this paper produces the highest amount of evolved hydrogen under 1 sun irradiation condition (100 mW/cm<sup>2</sup>, AM 1.5 G filter).

## EXPERIMENTAL PROCEDURE

### 1. Materials

Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O), cadmium nitrate tetrahydrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), copper(II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), and methyl blue (C<sub>37</sub>H<sub>27</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>3</sub>) were purchased from Aldrich and used without further purification. Ethanol was obtained from Duksan pure chemicals (C<sub>2</sub>H<sub>5</sub>OH), and deionized (DI) water (>18 MΩ) was used in all experiments.

### 2. Synthesis of ZnS-ZnO-CuS-CdS Heterostructured Photocatalyst

We fabricated a new type of heterostructured photocatalyst to

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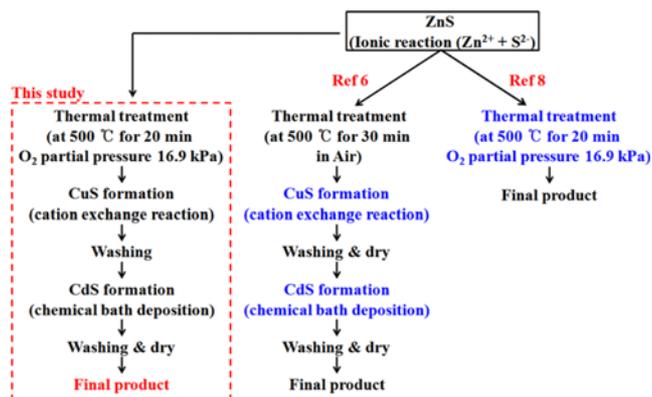


Fig. 1. Experimental procedures of this study in comparison with our previous works [6,8].

maximize the photocatalytic activities by incorporating four components (ZnS-ZnO-CuS-CdS). Basically, this study is based on our previous works [6,8] with slight modifications in the experimental procedures as shown in Fig. 1. Briefly, the ZnS nanoparticles were synthesized in ionic solutions ( $Zn^{2+}+S^{2-}$ ) from  $Zn(NO_3)_2 \cdot 6H_2O$  and  $Na_2S \cdot 9H_2O$  precursors. Then, the as-formed ZnS particles were thermally treated at 500 °C for 20 min under  $O_2$  partial pressure 16.9 kPa (ZnS-ZnO composite was formed). The gas flow rate (50  $cm^3/min$ ) and the heating rate (10 °C/min) were fixed during thermal processing. For synthesizing the ZnS-ZnO-CuS-CdS heterostructure, a sequential fabrication approach (ZnS→thermal treatment (ZnS-ZnO)→CuS formation (ZnS-ZnO-CuS)→CdS addition (ZnS-ZnO-CuS-CdS)) was used. For the first stage, the CuS components were introduced by cation exchange reaction ( $Cu(NO_3)_2 \cdot 3H_2O$  precursor: 10.35, 20.70, 31.05, 41.40, 51.75 and 62.10  $\mu mol$  using 2.07 mM ethanol solution) with 0.3 g ZnS-ZnO particles in 20 mL ethanol. For the second stage, the chemical bath deposition method ( $Cd(NO_3)_2 \cdot 4H_2O$  and  $Na_2S \cdot 9H_2O$  precursor: 0.125, 0.250, and 0.375 mmol in 100 mL DI-water individually, with as-synthesized ZnS-ZnO-CuS particles) was utilized to develop the ZnS-ZnO-CuS-CdS heterostructure as a final product.

### 3. Photocatalytic Reactions and Characterization

Photocatalytic reactions (hydrogen production, and methyl blue decomposition) were carried out in the same Pyrex glass reactor, which is a flat top cylindrical shape with 330 mL total volume under 1 sun irradiation condition (100  $mW/cm^2$ ) with a solar simulator (Pecel Technologies, PED-L11) equipped with 150 W Xe lamp and AM 1.5 G filter. The standard light intensity was carefully calibrated by using the Si photodiode (PEC cell, BS-520).

Hydrogen production activities of all samples were examined in 150 mL aqueous solution containing 0.1 g photocatalyst and 60 mM  $Na_2S \cdot 9H_2O$ . Prior to light illumination, the reactor was completely deaerated with  $N_2$  gas for 1 h. Total reaction time was 150 min, and the evolved gas was collected every 30 min with a gas-tight syringe and analyzed by a gas chromatograph (Chrompack, CP9001) equipped with a thermal conductivity detector and a 5 Å molecular sieve column.

Photocatalytic degradation experiments of organic dye were also conducted with 5 mg methyl blue in 150 mL aqueous solution containing 5 mg photocatalyst. For this experiment, methyl blue (5 mg)

was firstly dissolved into 100 mL DI water, and predetermined amount of photocatalyst (5 mg) was ultrasonicated with 50 mL DI water, individually. After above two solutions were mixed, they were stirred in the dark for 1 h to achieve adsorption-desorption equilibrium. Every 20 min, a sample was collected by centrifugation and characterized by UV-vis absorption spectrometer (Scinco, S4100) to analyze optical change of the dye solution. The room temperature photoluminescence (PL) measurements were performed on Acton Research Co, Spectrograph 500i with He-Cd laser source (325 nm).

## RESULTS AND DISCUSSION

The ZnS particle was synthesized as a base material by the ionic reaction ( $Zn^{2+}+S^{2-}$ ) for the subsequent photocatalysts fabrications. Thermal treatment of the pristine ZnS was applied to introduce ZnO component, and ZnS-ZnO-CuS-CdS heterostructured photocatalyst was manufactured by adding CuS and CdS components onto the preformed ZnS-ZnO surfaces for improving photocatalytic activities.

In our previous work [8], we reported that ZnO could be formed by thermal oxidation of the ZnS. During thermal process, both temperature and  $O_2$  partial pressure affect the amount of zinc oxide (ZnO) formed on the preformed ZnS surface, and the oxidation was confirmed by TGA-DTA, XRD, XPS and ICP-AES analyses (not shown in this study). At the optimal condition (at 500 °C under 16.9 kPa  $O_2$  partial pressure) for hydrogen production, the Zn/S/O atomic compositions were measured as 45.9/46.9/7.2 (XPS) and 53.3/42.1/4.6 (ICP-AES), respectively. Therefore, in this study thermal treatment condition was also applied to the same condition (500 °C under 16.9 kPa  $O_2$  partial pressure) as reported [8]. Light absorption of the ZnS-ZnO composite structure is increased by introducing the ZnO component, which has relatively small band gap energy, and electron-hole recombination can be effectively suppressed in the composite structure. As mentioned above, controlling the oxide content in the ZnS-ZnO composite is important to have improved photocatalytic activity, and thus the photoluminescence

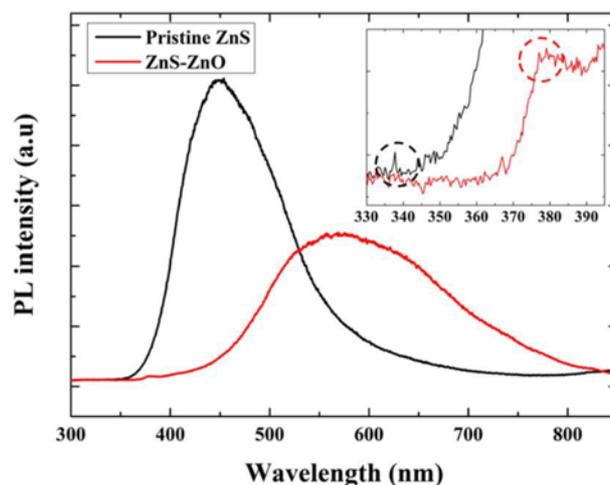


Fig. 2. PL spectra of pristine ZnS and thermally treated ZnS-ZnO composite. The intrinsic emissions of ZnS and ZnO are also shown in the inset.

(PL) measurement is conducted to examine the change of light emission from the pristine ZnS and the ZnS-ZnO composite. Fig. 2 shows PL spectra of the pristine ZnS and thermally treated ZnS-ZnO composite. Generally, the intrinsic emissions of ZnS and ZnO are located around 337 nm and 376 nm, respectively, but these peaks are not notable in this study. Instead, strong and broad peaks associated with lattice vacancies from S and O atoms are observed in Fig. 2 as reported in other researches [9,10], compared with the intrinsic emission peaks. This lattice vacancy is mainly attributed to the crystal defects of nanoparticles with high specific surface area. Fig. 2 demonstrates the shift of the characteristic emission peak by forming the ZnO component on the ZnS surface. This result further indicates that photogenerated electrons and holes are not re-combined in ZnS species, and thus they are efficiently separated in the ZnS-ZnO composites.

Utilizing the ZnS-ZnO composite structure, CuS and CdS components are sequentially introduced for further improvement of photocatalytic activity. Various compositions of the ZnS-ZnO-CuS-CdS heterostructured composite are explored for hydrogen production, and Table 1 summarizes the synthesis conditions of the photocatalysts and their hydrogen production activities under 1 sun irradiation condition. Hydrogen production rates of the heterostructured samples are higher than that of the ZnS-ZnO composite ( $494.8 \mu\text{mol g}^{-1} \text{h}^{-1}$ ), and the hydrogen production rate is strongly dependent on the amount of CuS and CdS additions. In our previous work [6], we reported that each component (CuS and CdS) plays an individual role and its composition is a crucial factor to improve hydrogen production in the heterostructure system. In addition, the optimized composition of the heterostructure system is also much dependent on the formation of ZnO component. This is because electron-hole generation, charge separation, and electron movement can be totally changed with photocatalytic systems. Therefore, optimal composition for additional components should be established in examining photocatalytic hydrogen productions.

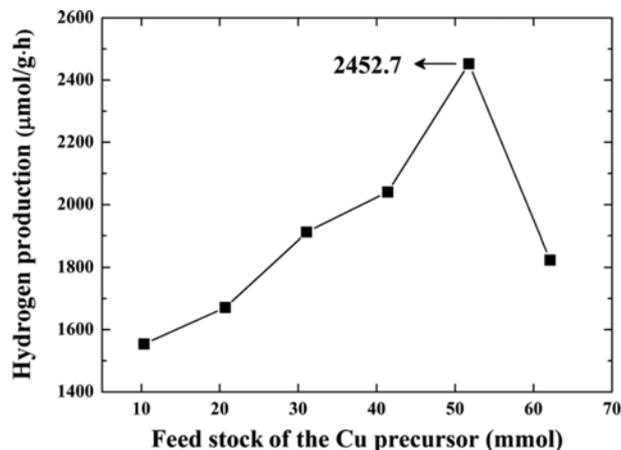
**Table 1. Synthesis conditions of the thermally treated ZnS and the ZnS-ZnO-CuS-CdS composite photocatalysts from 18 different feed stocks of the precursors ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ). Hydrogen productions are averaged for 150 min under 1 sun irradiation containing 0.1 g photocatalyst and 60 mM  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$**

Feed stock			H <sub>2</sub> production ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )
ZnS <sup>a</sup> (g)	Cu <sup>b</sup> ( $\mu\text{mol}$ )	Cd <sup>c</sup> (mmol)	
0.3	-	-	494.8
0.3	10.35		1106.6/1554.0/1086.8
0.3	20.70		1361.8/1671.1/1564.3
0.3	31.05	0.125/0.250/0.375	1495.9/1911.8/1770.6
0.3	41.40		1620.6/2040.5/1880.6
0.3	51.75		1995.0/2452.7/2011.2
0.3	62.10		1451.8/1823.6/1598.1

<sup>a</sup>Thermally treated ZnS at 500 °C under 16.9 kPa O<sub>2</sub> partial pressure

<sup>b</sup>Amount of Cu precursor ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ )

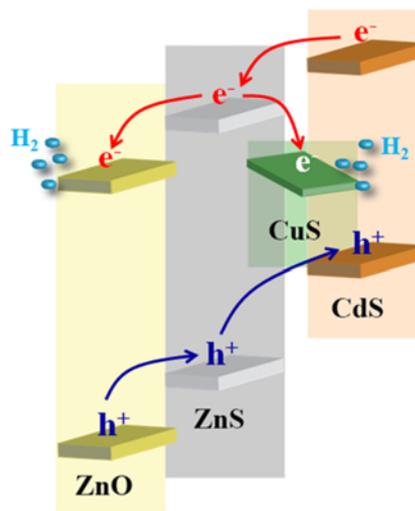
<sup>c</sup>Amount of Cd precursor ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), feed stock ratio between  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  precursor is 1 : 1



**Fig. 3. Hydrogen production from ZnS-ZnO-CuS-CdS photocatalyst as a function of Cu precursor content at 0.250 mmol Cd and S precursors.**

Among ZnS-ZnO-CuS-CdS heterostructure with various amounts of Cu precursor (from 10.35  $\mu\text{mol}$  to 62.10  $\mu\text{mol}$ ), the hydrogen production of all samples is the highest at the 0.250 mmol Cd precursor feed stock as shown in Table 1. Fig. 3 expresses the hydrogen production rates as a function of Cu precursor feed stock at 0.250 mmol Cd precursor feed stock. The hydrogen production from the ZnS-ZnO-CuS-CdS photocatalyst shows the highest value ( $2452.7 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) at 51.75  $\mu\text{mol}$  and 0.250 mmol Cu and Cd precursor feed stocks, respectively. This hydrogen production is about five-times higher than that from only the ZnS-ZnO composite. It is mainly due to the synergistic effects of charge separation and electron-hole movements in the heterostructured photocatalyst at this composition.

A schematic diagram of relative band energy positions in the ZnS-ZnO-CuS-CdS photocatalyst is represented in Fig. 4. The CdS has relatively narrow band gap energy, and so it can absorb the large amount of photons from solar irradiation. Thus, many electron-



**Fig. 4. Schematic band energy diagram and charge flow in the ZnS-ZnO-CuS-CdS heterostructured photocatalyst.**

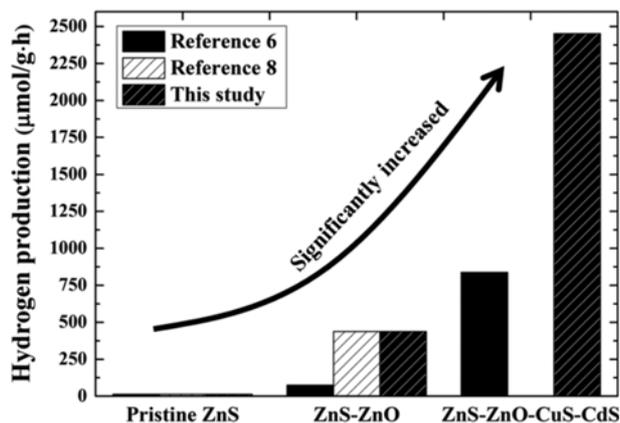


Fig. 5. Hydrogen production from pristine ZnS, ZnS-ZnO, and ZnS-ZnO-CuS-CdS photocatalysts compared to the previous researches [6,8].

hole pairs are generated from the CdS incorporated compound, and the generated electrons are transferred from CdS to CuS and ZnO, as shown in Fig. 4, because electrons in the conduction band of semiconductor flow from negative to positive direction. On the contrary, holes in the valence band flow opposite side (to CdS). Thus, effective charge separations of electron-hole pairs are possibly achieved in this heterostructure system, and it can also suppress the electron-hole recombination. In addition, it is important to keep the balance between generating and consuming electrons in order to maximize the hydrogen production, and in this point of view there is an optimal composition for the heterostructured photocatalysts.

Fig. 5 shows the results of the hydrogen production from pristine ZnS, ZnS-ZnO, and ZnS-ZnO-CuS-CdS photocatalysts compared to the previously reported values [6,8]. The pristine ZnS (not thermally treated) has very low photocatalytic activity ( $13.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) in all cases because of its relatively large band gap energy and low crystallinity. By thermal treatment at  $500^\circ\text{C}$  in air condition, the ZnS-ZnO composite is formed with increased crystallinity, and so hydrogen production [6] was increased up to  $75.0 \mu\text{mol g}^{-1} \text{h}^{-1}$ . Besides, hydrogen production [8] was much improved to  $438.4 \mu\text{mol g}^{-1} \text{h}^{-1}$  from the oxide content optimized ZnS-ZnO composite formed at  $500^\circ\text{C}$  and  $16.9 \text{ kPa O}_2$  partial pressure. After optimization of the oxide content in the ZnS-ZnO composites, in this study the CdS and CuS components were additionally introduced as light sensitizer and cocatalyst, respectively. As a result, the hydrogen production from the oxide optimized ZnS-ZnO-CuS-CdS heterostructure is  $2452.7 \mu\text{mol g}^{-1} \text{h}^{-1}$ , and it is about 180 times higher than that from the pristine ZnS. In addition, the hydrogen production rate ( $837.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ , [6]) from the ZnS-ZnO-CuS-CdS heterostructured with no oxide content optimization is lower than the current result. Therefore, it is important to use optimum component composition to fabricate heterostructured photocatalyst in order to achieve the best performance of the materials. To the best of our knowledge, it shows the highest value of hydrogen production from particulate photocatalyst system under 1 sun irradiation condition.

To demonstrate the potential application of the ZnS-ZnO-CuS-CdS photocatalyst, photocatalytic degradation activities for the methyl

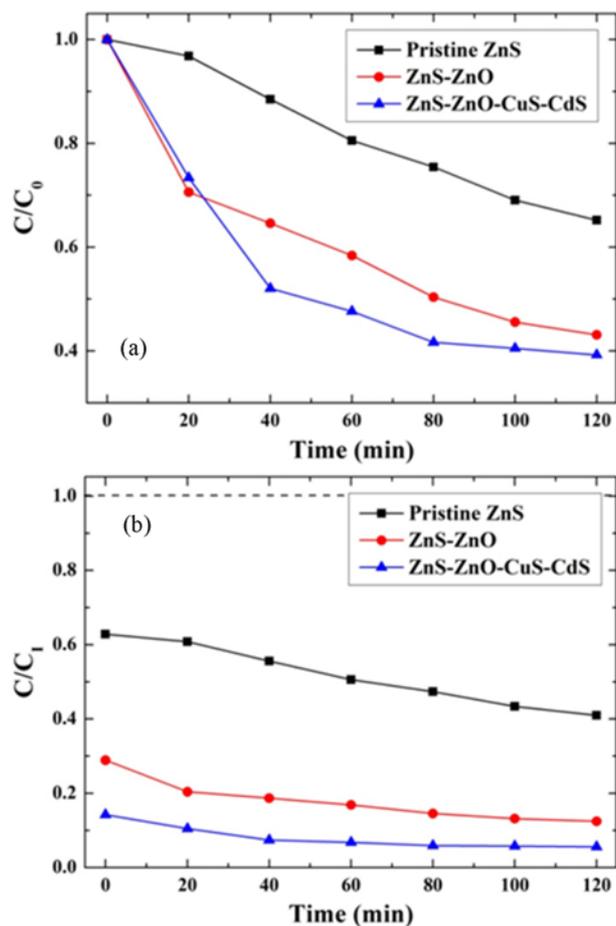


Fig. 6. Photodegradation of MB with pristine ZnS, ZnS-ZnO and ZnS-ZnO-CuS-CdS photocatalysts. The degradation plot is based on (a) the adsorption equilibrium concentration ( $C_0$ ) and (b) the initial solution concentration ( $C_i$ ) as a function of time.

blue (MB) were analyzed in addition to the hydrogen production from water splitting reaction. Photocatalytic decompositions of the organic dyes have also been studied to remediate the contaminated water containing toxic dyes to microorganisms, aquatic life and human beings [11].

The initial concentration of MB solution ( $5 \text{ mg}/150 \text{ mL}$ ) is used as a reference ( $C_i$ ) from UV measurement, and the concentration after adsorption equilibrium in the dark is  $C_0$ . After the adsorption equilibrium, the adsorbed MB molecules start to decompose under light irradiation. Fig. 6(a) represents photodegradation behaviors of photocatalysts based on the equilibrium concentration. The ZnS-ZnO-CuS-CdS photocatalyst shows the highest activity, and it is a similar result in the hydrogen production as shown in Fig. 5. In Fig. 6(b), the MB solution concentrations are normalized by  $C_i$ , and it demonstrates the difference of the adsorbed amount of MB molecules on the catalyst surfaces. For example, the ZnS-ZnO-CuS-CdS photocatalyst has the highest amount (about 86%) of adsorbed dye molecules, and these adsorbed dyes can further influence the photodegradation activity. Therefore, the multicomponent heterostructure can be used as an effective photocatalyst platform in degradation of organic contaminants as well as in generation of solar

hydrogen.

## CONCLUSIONS

Solar hydrogen production and organic dye decomposition were studied with heterostructured photocatalysts. Photocatalytic hydrogen production mainly utilizes electrons as major reaction carriers, and organic dye decomposition is a hole consuming process. We demonstrate that the ZnS-ZnO-CuS-CdS heterostructure has excellent photocatalytic activity on photocatalytic hydrogen production and dye degradation under 1 sun irradiation. To develop content optimized ZnS-ZnO-CuS-CdS photocatalyst, thermal processing condition and precursor feedstock are considered as crucial control parameters. The optimal composition of heterostructured photocatalyst was synthesized with 51.75  $\mu\text{mol}$   $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.250 mmol  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  based on 0.3 g ZnS sample thermally treated at 500 °C under 16.9 kPa  $\text{O}_2$  partial pressure. From this sample, the hydrogen production is 2452.7  $\mu\text{mol g}^{-1} \text{h}^{-1}$  and the MB decomposition is much faster than the other cases. This improved photocatalytic activity is mainly due to the suppressed charge recombination process by efficient charge separations in heterostructured materials.

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