

## THE INFLUENCE OF CADMIUM PRECURSORS UPON PdS/Zn<sub>1-x</sub>C<sub>x</sub>S PHOTOCATALYSTS EFFICIENCY IN WATERSPLITTING REACTION

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### Abstract

Photocatalysts based on hexagonal cadmium sulfide have been hydrothermally synthesized using crystalline zinc sulfide as sulfide source, and metal nitrates, acetates, chlorides and sulfates as cadmium sources. The powders have been characterized by X-Ray Diffraction (XRD), UV-VIS Diffuse Reflectance Spectroscopy (DSR) and Energy-Dispersive X-ray Spectroscopy (EDX). Further experiments of photocatalysis in aqueous solution of sulfide and sulfite for hydrogen evolution, were conducted. The samples were irradiated by monochromatic blue light, generated by an LED. From these experiments it was concluded that the presence of sulfate and acetate anions in the system results in more performant photocatalysts than the presence of nitrate and especially chloride anions.

### Introduction

The increasing demand for new, environment friendly energy sources opens the opportunity for hydrogen production by photocatalytic water splitting. Currently scientific and industrial interest is focused on the capability of materials (photocatalysts) to absorb light especially in the visible range, which represents about 43% of the solar spectrum [1]. The highly negative potential of excited electrons in the conduction band and the rapid generation of electron-hole pairs by incident photon provides a high photocatalytic activity to the zinc sulfide based compounds [2]. Using dual/coupled systems such as ZnS-CuS, ZnS-WS<sub>2</sub>, ZnS-CdS [2] composites or doping with Cd [3], represents a common way for shifting the wide band gap energy of ZnS (3.35 eV) to visible region. In the case of dual semiconductor photocatalysts the charge separation mechanism consists in the injection of electrons from one of the semiconductors into the conduction band of the second semiconductor [4].

The aim of this study was the comparison of the photocatalytic efficiency of PdS/CdS-ZnS composite compounds obtained from different cadmium salts.

### Experimental

#### ZnS precursor synthesis

ZnS is precipitated by the addition of a Na<sub>2</sub>S solution in an acidified aqueous solution of ZnSO<sub>4</sub>. The S<sup>2-</sup>:Zn<sup>2+</sup> molar ratio used in the precipitation was 0.9. Due to the acid environment, the Zn(OH)<sub>2</sub> precipitation is excluded. ZnS was then washed with distilled water and placed in an autoclave which was heated for 20 hours at a temperature of 200°C to improve the crystallinity. Crystallized Zn sulfide was washed twice with water and the last time with ethanol, then dried in vacuum at 60°C. XRD spectra revealed the existence of cubic ZnS phase.

#### Photocatalysts synthesis using different Cd<sup>2+</sup> salts as precursors

290 mg of crystallized ZnS was dispersed by 30 minutes sonication in 30 ml of bidistilled water. In the resulted suspension, 1 ml of glacial acetic acid was added, under constant stirring. After 5

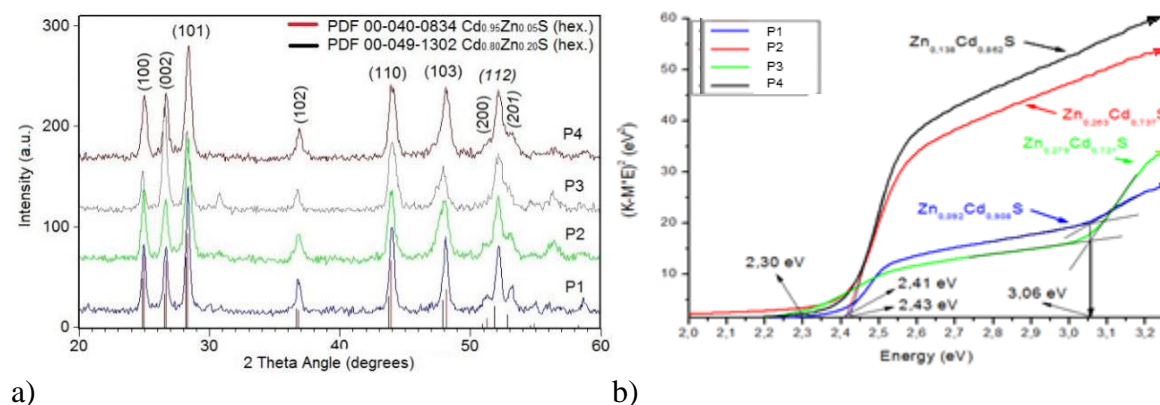
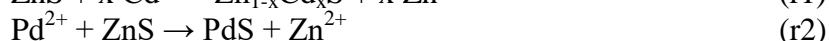
minutes, 4 mL  $K_2PdCl_4$  with a concentration of 0.6 mg/mL  $Pd^{2+}$ , was added. After 2 minutes of stirring, 2 mmols of cadmium salt were added in each autoclave, to achieve the same Zn : Cd atomic ratio. The suspensions were subjected to hydrothermal treatment at 200°C for 70 hours. After the hydrothermal treatment, the powders were separated by filtration, washed with distilled water and were kept in  $Na_2S$  0.2 M solution.

### Photocatalysis

For the conducted photocatalysis experiments, in each particular case, a variable volume of photocatalyst suspension was taken in order to obtain a final mass of 25 mg photocatalyst. The reaction volume was brought to 25 mL and the  $S^{2-}$  ion concentration to 0.2 M. By adding sodium sulfite the  $SO_3^{2-}$  concentration was brought to 0.1 M. The reactions were conducted at 25°C and the suspension was irradiated with 400 nm blue light. The determination of the amount of released hydrogen was done volumetrically.

### Results and discussions

The main reactions that occurred during the hydrothermal treatment are the following:



**Fig. 1.** The XRD spectra of P1-P4 samples (a) and the band gap values for various photocatalysts (b).

It was observed that r2 reaction takes place at high speed even at room temperature, leading to immediate changes in color of ZnS suspension from white to brown. This change takes place in the presence of  $Pd^{2+}$  ions, which also highlights the formation of PdS. The process takes place due to lower solubility of the PdS in comparison to CdS and ZnS. Stoichiometry of the compounds was determined from EDX analysis and is presented in Table 1. Both XRD (Fig. 1a) and UV-VIS spectra (not shown here) demonstrates the presence of dual phases in P3 which are a mixture of ZnS cubic phase and hexagonal  $Zn_{1-x}Cd_xS$  solid solution. In conclusion, the reaction product is a mixture of  $Zn_{1-x}Cd_xS$  and unreacted ZnS, the amount of unreacted ZnS being dependent on the used cadmium salt. In comparison to other samples which are preferentially oriented to 101 direction, P3 shows a preferential growth to 002 direction. Regarding the photocatalytic performance, P3 shows the lowest activity.

**Table 1**

No.	Cd precursor	Zn precursor	Composition obtained by the EDX analysis	Photocatalyst code
1	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	ZnS	$\text{Zn}_{0.092}\text{Cd}_{0.908}\text{S}$	P1
2	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	ZnS	$\text{Zn}_{0.263}\text{Cd}_{0.737}\text{S}$	P2
3	$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$	ZnS	$\text{Zn}_{0.279}\text{Cd}_{0.721}\text{S}$	P3
4	$\text{CdSO}_4 \cdot 8/3$	ZnS	$\text{Zn}_{0.138}\text{Cd}_{0.862}\text{S}$	P4

The band gap values,  $E_g$ , were determined from DSR spectra. As shown in figure 1b, the P1 and P3 samples have two band gap values indicating two different compounds. Regarding P1 sample, the band gap value of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  compound is around 2.41 eV. Also a small amount of ZnS is visible in diffuse reflectance spectra (not shown here); however, in case of sample P3 a larger amount of ZnS was detected.  $E_g$  value of unreacted ZnS, which was probably Cd-doped, was about 3.06 eV in both cases, with slightly decreased value compared to the pure cubic crystallized ZnS which is about 3.55 eV.

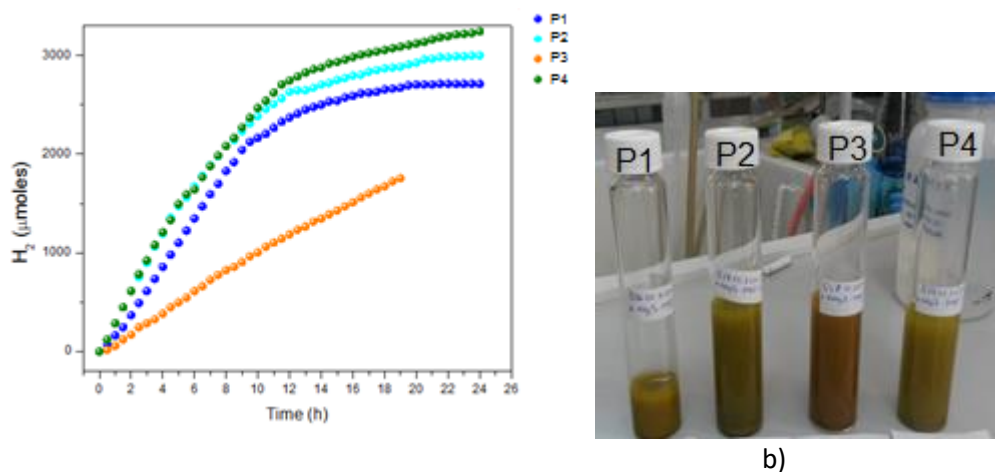
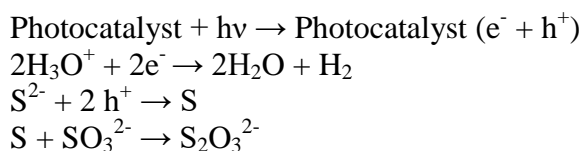


Fig. 2. Hydrogen evolution curve for various environments synthesized photocatalysts (P1 –  $\text{NO}_3^-$ , P2-  $\text{CH}_3\text{COO}^-$ , P3 –  $\text{Cl}^-$ , P4- $\text{SO}_4^{2-}$ ) – a) and the image showing the suspensions of the used photocatalysts – b)

As shown in the figure 2a, in the first two hours of illumination, the evolution rate of hydrogen increases progressively. Between 2 and 8 hours, the hydrogen evolution rate is relatively constant, with a decline after more than 8 hours of illumination. The decreasing rate of hydrogen production is due to the decrease of sodium sulfite concentration in the solution. In the absence of sodium sulfite, the sulfide ion is oxidized to sulfur. It reacts with excess of sodium sulfide producing polysulfide ions. The polysulfide solution is yellow, which means that it absorbs blue light emitted by the LED. The main reactions that take place are:



As seen from the above reactions, in order to obtain one millimole of hydrogen it is required to use 1 mmol of sodium sulfite before the beginning of the sodium polysulfide formation. Because 2.5 mmol sulfite was introduced in the reaction, we can expect to observe reaction speed reduction after the 2.5 mmol of hydrogen production. Indeed, in figure 2a we can see that after the release of 2-2.5 mmol hydrogen, the hydrogen production rate drops steeply due to the formation of polysulfide which can be observed visually (yellow solution) as well, after the photocatalyst filtration.

### **Conclusion**

The obtained photocatalysts are mixtures of ZnS and  $Zn_{1-x}Cd_xS$  (where  $x$  is close to 1) the amount of unreacted ZnS salt depending on the nature of the used cadmium salt. The photocatalytic experiments were conducted under monochromatic light (400 nm). According to the XRD, DSR and EDX analyses, in the presence of chloride ions, the ZnS reactivity is minimal leading to the formation of the lowest performance photocatalyst. The presence of sulfate and acetate anions in the system, may be the reason for obtaining higher performance photocatalysts.

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