New synthesis method of cheap and highly efficient $PdS/Zn_{1-x}Cd_xS$-type photocatalysts for hydrogen production

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A new method using wastes and hydrothermal treatment for obtaining highly efficient $PdS/Zn_{1-x}Cd_xS$-type photocatalysts for hydrogen production is presented. The use of a Cd precursor recovered from used battery wastes and of a one-step hydrothermal synthesis in a hermetic system (teflon autoclave) and relatively low temperature (up to 200°C) have provided a low-cost and ecological production of $PdS/Zn_{1-x}Cd_xS$ photocatalysts. The photocatalysts obtained by this method have good stability and relatively high efficiency which increases significantly with temperature (about 3.53 mmol/g·h at 25°C, 3.77 mmol/g·h at 40°C and 5.97 mmol/g·h at 60°C under continuous 1.28 W irradiance).

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1. Introduction

Hydrogen fuel is regarded as one of the most promising clean and sustainable energy resources in the near future. Among the multiple ways for solar hydrogen production (electrolysis of water using a solar cell, reforming of biomass, photocatalytic or photoelectrochemical water splitting - artificial photosynthesis, etc), photocatalytic water splitting could contribute to an ultimate green sustainable chemistry [1]. Photocatalytic water splitting using sunlight needs the development of highly efficient and cheap photocatalysts active in visible. One such category are the CdS-based photocatalysts which, in some configurations, can achieve extremely high quantum efficiencies (up to 93%) in photocatalytic hydrogen production in the presence of sacrificial reagents under visible light irradiation, showing very good stability under the photocatalytic reaction conditions [2 - 4]. Also, $Cd_{1-x}Zn_xS$–type (CZS) solid solution photocatalysts with good performances have been developed [5, 6].

The information found in the literature regarding methods for the synthesis of CZS, i.e., by sulfiding the mixture of oxides [5], by precipitation at ambient pressure or by reaction of metal salts with H_2S gas [7], by co-precipitation from the acetates of metals in inert environment [8], hydrothermally by co-precipitation of metals with the sulfide ions obtained by the decomposition of the thiourea [9, 10], relates to methods of synthesis that involve high synthesis temperatures, sometimes a lesser degree of crystallinity of the product, several process steps or extreme conditions (emission of toxic H_2S, vapors of cadmium or volatile salts) that causes a high wear of the synthesis equipment, hazardous working conditions, but also high final cost of the visible active photocatalysts.

In this paper we present a new single step greener synthesis method which allows to obtain highly efficient visible active photocatalysts type $PdS/Zn_{1-x}Cd_xS$ (PZCS) with high crystallinity and low production costs by using low purity precursors recovered from batteries industry wastes and one-step hydrothermal treatment.

2. Experimental

2.1. Preparation of cadmium precursor

For the preparation of the cadmium precursor it is first necessary the physical separation of the components of the battery (cathode, anode, steel, current collectors, and separators - Fig. 1).

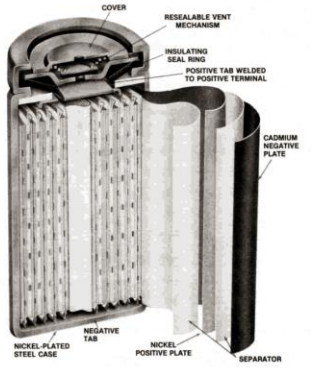

Fig. 1. Ni-Cd battery (section view) [11]

The main component of cadmium salts present in the composition of the batteries anode is cadmium hydroxide. This compound is contaminated with nickel, iron, carbon and other trace elements (Fig. 2). In case of PCZS-type photocatalysts synthesis, it is necessary and sufficient one stage mechanical separation of cadmium hydroxide from the steel reinforcement of Ni-Cd-type batteries anode, without any further purification.

2.2. Single step hydrothermal synthesis of $PdS/Zn_{1-x}Cd_xS$-type photocatalysts

In a typical synthesis procedure, 563 mg ZnS was suspended in 50 mL water by sonication for 30 minutes. 3 mL glacial acetic acid was added and stirred for 5 minutes then 2 mg of $PdCl_2$ in 30 ml of water sonicated for 10 minutes was added. Over this mixture 500 mg of cadmium waste was added and sonicated for 10 minutes (10s US, 10s pause). After adding the palladium salt the suspension gets a slightly brown hue.

Chemical equation 1 describes the general process of ion exchange between zinc and cadmium underlying the synthesis of $PdS/Zn_{1-x}Cd_xS$-type photocatalysts.

$$ZnS + x\ Cd^{2+} \rightarrow Zn_{1-x}Cd_xS + x\ Zn^{2+} \quad (1)$$

$$ZnS + Pd^{2+} \rightarrow PdS + Zn^{2+} \quad (2)$$

Since PdS ($K_{sp} = 2 \times 10^{-58}$) is much less soluble than ZnS ($K_{sp} = 3 \times 10^{-24}$) or CdS ($K_{sp} = 1 \times 10^{-27}$), PdS will immediately precipitate in a suspension of ZnS or CdS, according to reaction 2.

The slurry was then transferred into a stainless steel autoclave lined with PTFE and, after closing, it was placed into an oven preheated to 200°C and maintained for 72 h at that temperature. The product was then washed with water and ethanol and dried in vacuum at 60°C for 1 h.

2.3. Characterization

Structural characterization of the photocatalyst samples was performed by powder X-ray diffraction (XRD) using an X'Pert Pro MPD diffractometer with CuK-alpha radiation. The morphological and compositional characterization was performed using FEI-Inspect S scanning electron microscope and EDX detector within the system. Optical properties were determined with a PerkinElmer Lambda 950 UV-Vis-NIR spectrometer using the 150 mm integrating sphere module for diffuse reflectance measurements.

2.4. Photocatalysis experiments

Photocatalytic hydrogen production experiments were performed using 100 mg of photocatalyst type PdS(0.2% by weight)/$Zn_{0.2}Cd_{0.8}S$ dispersed in 300 mL of 0.5M Na_2S and 0.25M Na_2SO_3 aqueous solution. Illumination was done with simulated solar light, produced by an Oriel solar simulator equipped with AM 1.5 type radiation filter and 250 W xenon lamp. The illuminated surface area was about 12.8 cm^2. The irradiance has been measured by a calibrated solar cell and was 100 mW/cm^2. The temperature was maintained constant by introducing the photoreactor in a glass parallelepiped in which the temperature was controlled with a thermostatic bath. Photocatalysis experiments were performed at different temperatures (25, 40 and 60°C).

3. Results and discussion

3.1. Cadmium precursor

According to EDX analysis, cadmium hydroxide is contaminated mainly with nickel (2.6%), carbon (6%) and possibly traces of selenium (Fig. 2). The source of cadmium is a gray powder and it can be used as such in the hydrothermal synthesis step, not requiring any purification in order to remove other metals. This makes the price of production of CZS-type photocatalysts to be particularly low.

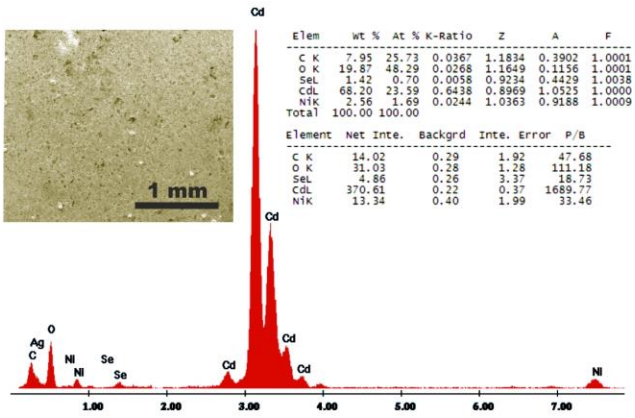

Fig. 2. EDX spectrum of recovered Cd waste from Ni-Cd batteries (insets: left- SEM image of surface used for EDX; right – quantification of elemental composition)

3.2. The photocatalyst

In Fig. 3, the XRD patterns for $Zn_{0.2}Cd_{0.8}S$-type photocatalyst compared to a sample rich in Cd ($Zn_{0.04}Cd_{0.96}S$, prepared under similar conditions) are presented. The diffraction peaks of all samples were well-indexed to the CdS hexagonal (JSPDS card NO. 00-041–1049). No peaks of any impurities are observed. The right shift of the diffraction peaks with increasing Zn content is due to the replacement in different proportions of Cd^{2+} ions by Zn^{2+} ions having more reduced volume. The absence of other secondary crystalline phases in the XRD profile certifies that by this method can be obtained high purity solid solutions in the ZnS - CdS system.

SEM image (Fig. 4) reveals that the obtained product is nanocrystalline, with crystalline grains sizes ranging from tens to hundreds of nanometers.

Fig. 5 presents the EDX spectra for cadmium-based waste (black line) and the $Zn_{0.2}Cd_{0.8}S$-type solid solution photocatalyst (green line). It is clear that in the course of hydrothermal treatment, nickel salts remain in the electrolyte solution and cadmium cations replace zinc ions in the zinc sulphide structure.

The PdS/$Zn_{0.2}Cd_{0.8}S$-type photocatalyst has yellow-brown color and a band gap value determined from UV-Vis-NIR diffuse reflectance spectra of about 2.39 eV (Fig. 6), completely absorbing blue and part of the green components of solar spectrum.

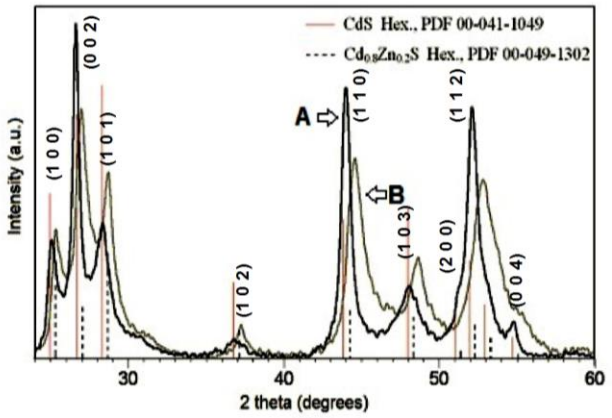

Fig. 3. Comparative XRD profiles for photocatalysts type $Zn_{0.04}Cd_{0.96}S$ (A) and type $Zn_{0.2}Cd_{0.8}S$ (B)

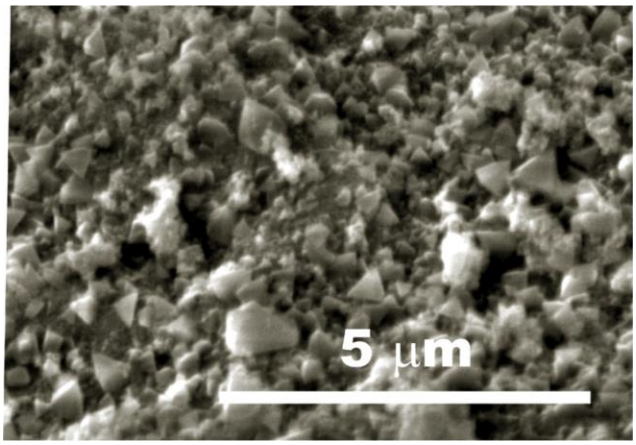

Fig. 4. SEM image of the $Zn_{0.2}Cd_{0.8}S$-type photocatalyst

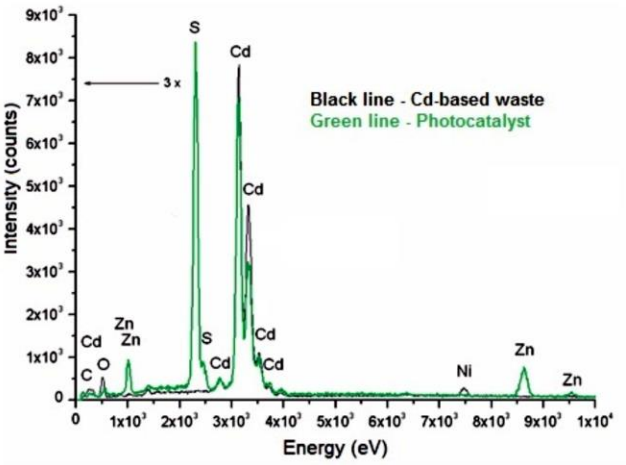

Fig. 5. EDX spectra for cadmium-based waste (black line) and $Zn_{0.2}Cd_{0.8}S$-type photocatalyst (green line)

3.3. Photocatalysis experiments

The results of temperature-dependent photocatalytic hydrogen production experiments using 100 mg photocatalyst type 0.2%PdS/$Zn_{0.2}Cd_{0.8}S$ suspended in 300 ml of 0.5M Na_2S + 0.25M Na_2SO_3 aqueous solution at 25, 40 and 60°C with simulated AM1.5 solar light illumination, are shown in Fig. 7.

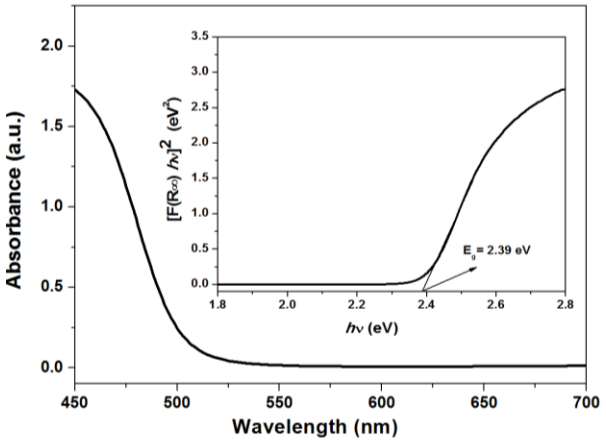

Fig. 6. The variation of absorption coefficient with wavelength and insert shows the corresponding energy band gap (Eg) of the PdS/$Zn_{0.2}Cd_{0.8}S$ photocatalyst

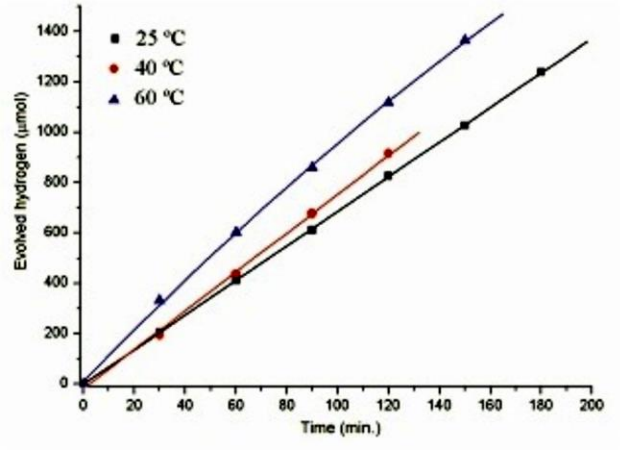

Fig. 7. Hydrogen evolution rate on photocatalyst type 0.2%PdS/$Zn_{0.2}Cd_{0.8}S$ suspended in 0.5M Na_2S + 0.25M Na_2SO_3 aqueous solution, at 25, 40 and 60°C, using simulated AM1.5 solar light illumination

The photocatalysts obtained from wastes show good photocatalytic activity even at 25°C under illumination with simulated sunlight, of about 3.53 mmol/g·h. The rate of hydrogen evolution is about 3.77 mmol/g·h at 40°C and 5.97 mmol/g·h at 60°C under continuous 1.28 W irradiance. The activity of photocatalyst is stable along the photocatalysis experiments (at least hundreds of minutes).

The 0.2%PdS/$Zn_{0.2}Cd_{0.8}S$ photocatalyst prepared from wastes by our method shows comparable performances with the 1%PdS/CdS-type highly efficient photocatalyst prepared from analytical grade precursors by Yan et al. [3].

So, we demonstrated a new ecological one step synthesis method for cheap PdS/$Zn_{1-x}Cd_xS$-type relatively high efficiency photocatalyst using impure Ni-Cd battery wastes as Cd precursor.

4. Conclusions

A new eco-friendly method using wastes and one-pot low temperature hydrothermal treatment for obtaining cheap and highly efficient PdS/$Zn_{1-x}Cd_xS$-type photocatalysts for hydrogen production was demonstrated. The method allows the direct use of cadmium hydroxide wastes from used Ni-Cd batteries as cadmium precursor in the hydrothermal synthesis reaction of the photocatalysts.

The 0.2%PdS/$Zn_{0.2}Cd_{0.8}S$ photocatalysts obtained from wastes are stable along the photocatalysis experiments (at least hundreds of minutes) and show increasing efficiency with temperature rise from 25 to 60°C, being comparable with highly efficient photoctalysts type 1%PdS/CdS reported in the literature.

Acknowledgements

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