Generation of H_2 as renewable energy from cobalt doped ZnS as photocatalyst under UV light

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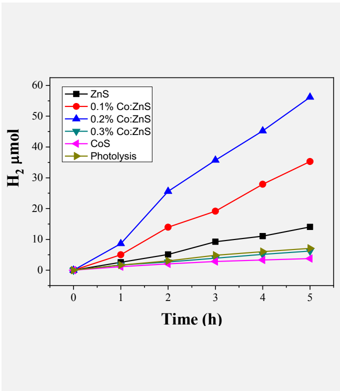

ZnS-doped cobalt-based photocatalysts were synthesized by the solvothermal synthesis method with different low cobalt contents within ZnS (0.1, 0.2, and 0.3 mol %). Furthermore, the undoped bare materials ZnS and CoS were prepared to compare their efficiency with those mentioned above in generating renewable energy by photocatalysis. The photocatalytic behavior of all catalysts was carried out under UV illumination (254 nm) using a 1:1 solution by volume of water/methanol. It was shown that the 0.2% Co:ZnS material generated about 60 µmol of H_2 after 5 h of photocatalytic reaction, while undoped ZnS and CoS showed lower H_2 generation. The main reason for this behavior may be that the insertion of cobalt into the ZnS structure promotes the generation of interband energy levels, decreasing the recombination of photogenerated electrons and holes.

Introduction

Clean and sustainable energy technologies are required in all sectors of the economy to decarbonize the world. Clean fuel production from water under ultraviolet-visible irradiation stands out significant innovation to shorten the growing amount of CO_2 and alleviate the worldwide reliance on non-renewable petroleum products [1].

Photocatalytic hydrogen production from water splitting provides a sustainable strategy to fulfill the future energy demand without environmental disruption, since hydrogen is a clean energy vector, while water and solar energy are inexhaustible [2].

ZnS is one of the most widely investigated photocatalysts because it rapidly generates electron-hole pairs under photoexcitation and exhibits a relatively high activity for H_2 production under UV light. ZnS has a hexagonal and cubic structure and forms nanosheets or nanorods with large specific surface area [3]. Therefore, in this work, the insertion of cobalt cations into the crystalline structure of ZnS was proposed to increase its photocatalytic efficiency in the H_2 production by photocatalytic methanol reforming.

Material and Methods

The materials were prepared by the solvothermal method, hydrozincite and thiourea were used as synthesis precursors to obtain ZnS, while for the cobalt doped ZnS photocatalysts, the appropriate amount of the reagent cobalt nitrate hexahydrate was added to obtain materials with a cobalt composition at 0.1, 0.2, and 0.3 % mol.

The amount of H_2 produced was quantified on a gas chromatograph GOW-MAC Series 580 equipped with a column of SiO_2 and a TCD detector. The photocatalytic reaction was carried out in a batch type reactor, the light comes from a mercury lamp (UV-Pen Ray) emitting at a wavelength of 254 nm. In each photocatalytic reaction, 50 mg of the photocatalyst were added to a solution composed of 75 mL of analytical-grade methanol and 75 mL of distilled water; the reaction was kept under continuous UV lighting and magnetic stirring. The hydrogen produced was analyzed by a TCD detector; then, the data was collected by the Clarity software. The micromoles of H_2 produced were quantified through a previously made calibration curve.

Results and Discussion

The synthesized photocatalysts were characterized by X-ray diffraction (see Figures 1 and 2). Figure 1 shows the typical reflection peaks of a cubic structure (sphalerite) for the ZnS and cobalt doped ZnS samples, while CuS has an amorphous structure.

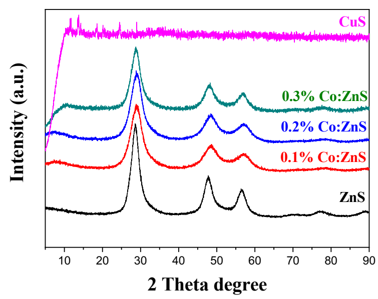

Figure 1. X-ray diffraction of ZnS, Co^{2+}-doped ZnS and CoS materials.

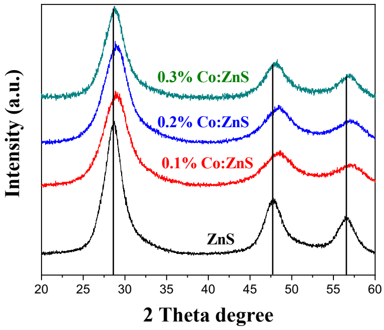

Figure 2. Shift of X-ray diffraction reflection peaks of cobalt doped ZnS materials.

The peaks observed in Figure 1 at approximately 28.4°, 47.3°, and 56.1° correspond to the (111), (220), and (311) planes, respectively. They were indexed to the crystallographic card PDF# 01-071-5976 for the ZnS cubic phase. The addition of cobalt into the cubic structure of ZnS is reflected in the slight shift of the peaks towards slightly higher values of two theta (Figure 2). It can be suggested that Co^{2+} cations are impurities within the ZnS structure.

All synthesized materials were assessed for their ability to produce H_2 through photocatalysis using methanol as a sacrificial agent. Figure 3 illustrates the amount of hydrogen in micromoles produced per gram of catalyst during a five-hour photocatalytic reaction.

The most active of the synthesized photocatalysts was the 0.2% Co:ZnS material with an H_2 production rate of 2454 μmol $H_2/g_{catalyst}$. It had a photocatalytic efficiency higher than the undoped-ZnS and CoS materials. The addition of Co^{2+} cations within the ZnS crystal lattice enhances the photocatalytic activity in H_2 production using a methanol-aqueous solution as demonstrated in Figure 3.

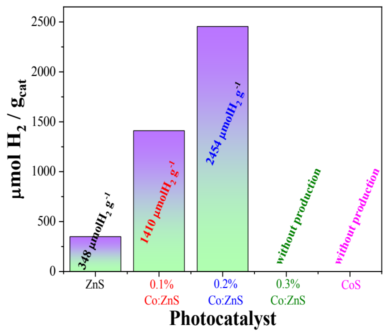

Figure 3. H_2 production rate of ZnS, cobalt doped ZnS and CoS materials.

Conclusions

The ZnS and Co^{2+}-doped ZnS materials were prepared using the solvothermal method and efficiently produced H_2 by photocatalysis. Inserting Co^{2+} into the cubic ZnS structure has been shown to promote higher hydrogen production compared to pure ZnS. On the other hand, CoS did not present any amount of H_2 produced. Perhaps, the insertion of cobalt into the ZnS structure promotes the generation of new interband energy levels near to conduction band of ZnS. These interband energy levels may function as an electron trap, decelerating the recombination rate of the hole-electron pair. As a perspective, some photoelectrochemical tests can give more information about the electron transfer during the photocatalytic reaction.

Acknowledgments

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