Chapter 6.   Hollow Microspheres of $Zn_xCd_{1-x}S$ Solid Solution with Noble-metal-free Co-catalysts for Hydrogen Evolution with High Quantum Efficiency in Visible Light

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Résumé

L'utilisation de l'énergie solaire pour produire de l'hydrogène à partir de l'eau est l'une des technologies clés qui traitent des problèmes d'énergie et d'environnement. Un photocatalyseur à petit gap avec une bonne séparation des charges et une grande stabilité peux jouer un rôle important dans ce processus. Récemment, le sulfate de zinc et de cadmium ($Zn_xCd_{1-x}S$) a attiré l'attention des chercheurs en raison de ses propriétés photocatalytiques uniques telles que sa large absorption du spectre lumineux visible et une forte stabilité lors de la production de dihydrogène. En outre, la caractéristique unique de ce semi-conducteur est sa capacité à modifier la distance entre ses bandes de conduction et de valence en modifiant le rapport Zn / Cd. Dans ce projet, une série de solution solide $Zn_xCd_{1-x}S$ a été synthétisée en utilisant du glycérol métallique suivi d'une calcination dans l'air et de la sulfuration dans un flux de H_2S. Cette nouvelle méthode a abouti à la création d'une solution solide homogène de wurtzite hexagonale qui pourrait produire une quantité massive d'hydrogène par absorption d'une grande partie de la lumière visible. En outre, l'application de MoS_2 en tant que cocatalyseur par la technique de la photo-dépôt, a généré la même quantité d'hydrogène que l'utilisation de Pt comme cocatalyseur. Les meilleurs résultats ont été obtenus par une solution solide $Zn_{30}Cd_{70}S$ qui pourrait générer plus de 12 $mmol.h^{-1}.g^{-1}$ sous la lumière d'un simulateur solaire. Il convient de mentionner qu'il existait des rendements quantiques très élevés ; 46,6% à 400 nm à 23,4% à 500 nm ainsi que 11,3% à 550 nm. Ils sont parmi les rendements quantiques les plus élevés qui ont déjà été signalés pour ce type de matériaux dans la région de la lumière visible.

Abstract

Utilizing solar energy in order to produce hydrogen from water is one of the key technologies to deal with energy and environment issues. A photocatalyst with a small band gap, good charge separation, and high stability plays an important role in this process. Recently, zinc cadmium sulfide ($Zn_xCd_{1-x}S$) has caught researchers' attention due to its unique photocatalytic properties such as the wide range of visible light energy absorption and strong stability during water splitting. Moreover, a unique feature of this semiconductor is the capability of modifying its band gap structure by changing the Zn/Cd ratio. Herein, a series of $Zn_xCd_{1-x}S$ solid solutions was synthesized by utilizing metal-glycerate followed by calcination in air and sulfuration under flowing H_2S. This new method resulted in a homogeneous hexagonal wurtzite solid solution that could produce a massive amount of hydrogen in a large range of visible light illumination. Moreover, applying MoS_2 as a cocatalyst via photo-deposition, generated the same amount of hydrogen as using Pt as a cocatalyst. The best results were obtained for the $Zn_{30}Cd_{70}S$ solid solution that could generate more than 12 mmol h^{-1} g^{-1} under solar simulator light. It exhibited very high quantum efficiencies; 46.6 % at 400 nm to 23.4% at 500 nm as well as 11.3% at 550 nm. There are among the highest QE that have been ever reported for this kind of material under visible light.

6.1 Introduction

No one can deny that the climate changes are happening due to global warming effects of greenhouse gases. One of the main reason for this crucial issue is the use of an immense amount of fossil fuels resulting in the massive emission of carbon dioxide into the atmosphere. One of the promising solutions for this problem is converting solar energy into hydrogen molecules via the photocatalytic process of water splitting. Honda and Fujishima were pioneers of splitting water into hydrogen and oxygen using TiO_2 under UV light.[6] However, the low efficiency of hydrogen production, which originates from absorption limited to the UV region, resulting in a limitation on its practical applications. This motivate many scientists to explore other efficient photocatalysts that can absorb the energy of visible light, which accounts for about 50% of sunlight energy.[77, 346, 347]

It has been established that CdS can act as a photocatalyst in hydrogen production reaction from water under visible light irradiation because of its narrow band gap and a proper conduction band position.[30, 348] The valence band of this metal sulfide is composed by S 3p orbitals located at higher energy levels, resulting in a narrow band gap with a strong visible light response.[269, 349] Nonetheless, its high photo-corrosion affects considerably its stability during photocatalysis reactions.[350] Various approaches have been investigated in order to improve the photocatalytic performance such as utilizing either a metal as co-catalyst or synthesizing composite materials with different elements.[23, 77, 351] Among these strategies, making solid solutions with other semiconductors is an interesting method to improve the photoactivity of CdS because of the ability to control the potentials of the conduction and valence bands of a solid solution by changing their compositions.[352]

$Zn_xCd_{1-x}S$ solid solution possesses an adjustable band gap width and a good resistance towards photo-corrosion.[353, 354] Moreover, this solid solution can produce hydrogen more efficiently than CdS alone, because its potential of conduction band edge is more negative than CdS.[352] Therefore, scientists and researchers have tried to synthesize it in various ways and enhanced its photocatalytic activities via different techniques.[19, 30, 77, 355, 356] Xing et al. synthesized $Zn_xCd_{1-x}S$ solid solution via a co-precipitation technique followed by thermal treatment.[357] They found that its band gap could be varied between 2.2 eV and 3.1 eV based on the value of x and the best hydrogen evolution was found with x = 0.2 that led to having a band

gap of 2.35 eV. Another group used thermal sulfuration method to enhance the activity of $Zn_xCd_{1-x}S$ solid solution for hydrogen production.[358] Furthermore, other methods such as doping or synthesizing nanoparticles of $Zn_xCd_{1-x}S$ solid solution have been used in order to improve its photocatalytic efficiency under visible light.[359-362] It should be mentioned that even the different crystal structures of $Zn_xCd_{1-x}S$ solid solution might affect its hydrogen evolution performance. For instance, hexagonal wurtzite $Zn_xCd_{1-x}S$ photocatalysts and cubic zinc-blend phase of this solid solution had various photocatalytic activities.[269, 270, 363] According to the literature, a photocatalyst with cubic zinc-blend phase showed significantly higher hydrogen production in comparison with hexagonal phase.[348, 352, 363] Interestingly, Liu et al. reported that $Zn_xCd_{1-x}S$ with nano-twinned structures could prevent the recombination of photoexcited carriers, resulting in considerably higher hydrogen evolution under visible light illumination.[270] Based on their observation, the photocatalyst with the help of Pt as a cocatalyst could generate 1.79 mmol of hydrogen with a QE of 43% at 425 nm. It is proved that defects in the structure of $Zn_xCd_{1-x}S$, could act as electron pools and so promote hydrogen production during photocatalytic water splitting.[270] However, the defect states in semiconductors should be controlled in order to obtain the maximum hydrogen evolution.

In this study, a series of $Zn_xCd_{1-x}S$ solid solutions were synthesized. By forming metal-glycerate of cadmium and zinc that were later converted to mixed oxides. The fact that the mixture consisted of two metal oxides which were homogeneously mixed together at atomic scale, made the mixture a good precursor for synthesizing a solid solution. This aim was achieved by further sulfuration by reaction with H_2S gas at high temperature. As a result, a highly activated solid solution of $Zn_xCd_{1-x}S$ was obtained that was surprisingly active under a large range of visible light illumination with a high quantum efficiency. This was one further step towards industrial application of this kind of photocatalysts. Moreover, depositing MoS_2 as a cocatalyst on the surface of this solid solution could allow producing as much hydrogen as using Pt. It is proved that platinum is one of the most efficient cocatalysts for photocatalytic hydrogen evolution reaction. However, its high cost and scarcity place some limitations on its usage especially for its large-scale applications. This usage of MoS_2 can lead to having a noble-metal-free photocatalyst with considerable quantum efficiency under visible light illumination.

6.2 Experimental section

6.2.1 Sample preparation

Zinc Cadmium sulfide solid solutions were synthesized as follows: First, glycerol and zinc nitrate and cadmium nitrate were dissolved in isopropanol and transferred into an autoclave. The autoclave was heated up to 180ºC for 6 h. During solvothermal treatment, microspheres of carbons were made from glycerol.[364] The microspheres contained numerous -OH$^-$ ions that provided a good capacity to absorb various cations specially Zn^{2+} and Cd^{2+}.[365] Later, the microspheres with adsorbed cations were collected via centrifugation and dried at 70ºC overnight. The obtained samples were calcined at 500ºC for 4 h yielding zinc and cadmium mixed oxide. Subsequently, the mixed oxide was exposed to a flowing gas mixture of H_2S (10%)/Ar at 450ºC for 2 h. Therefore, sulfide (S^{2-}) ions could substitute with oxygen and so the mixed oxide was converted to a mixed sulfide. Different atomic Cd/Zn ratios were used to synthesize of various compositions solid solutions which are noted as $Zn_xCd_{1-x}S$.

6.2.2 Characterization

TEM images of the samples were obtained with a JEOL JEM 1230 instrument operated at 120 kV. High-resolution TEM (HR-TEM) images were obtained by using JEOL JEM-2100F instrument operated at 300 kV. SEM images were obtained on a JEOL 6360 instrument operated at 15 kV. Powder XRD patterns were obtained on a Bruker SMART APEXII X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5418 Å). XPS measurements were carried out in an ion-pumped chamber (evacuated to 10^{-9} Torr) of a photoelectron spectrometer (Kratos Axis-Ultra) equipped with a focused X-ray source (Al Kα, hν = 1486.6 eV). The UV-Vis spectra were recorded on a Cary 300 Bio UV-visible spectrophotometer.

6.2.3 Photocatalytic test

The certain amount of photocatalysts (the optimum amount was 50 mg) was added to the 100 ml of an aqueous solution of 0.5M Na_2S and Na_2SO_3 as a sacrificial reagent. After that, the mixture was purged with nitrogen for 10 min and then under the solar simulator light (used for a deposition), co-catalyst was deposited via photo-deposition technique for 2 h. Then, the cell was purged again

with nitrogen for 30 min and the sample was ready for hydrogen production test during 3-hour cycles.

The quantum efficiency of the prepared sample was calculated according to follow equations[336]:

$$\text{Quantum Efficiency (QE)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$$

$$= \frac{2 \times \text{Number of evolved hydrogen molecules}}{\text{Number of incident photons}}$$

6.3 Results and Discussions

6.3.1 Material Characterizations

Figure 6.1 exhibited XRD analysis of samples after specific stages. It is clear that air calcination after sample synthesis provides a mixed oxide of CdO and ZnO that coexist together in two separate phases. According to the references, ZnO has a hexagonal crystal structure, whereas CdO crystal structure is a cubic one. After H_2S treatment, oxygen was replaced by sulfur and thus solid solutions of $Zn_xCd_{1-x}S$ were obtained (Figure 6.1-B). The XRD peaks of $Zn_{0.9}Cd_{0.1}S$ were very close to index peaks of hexagonal wurtzite phase of ZnS (JCPDS No. 00-003-1093).[270] It seems that in this concentration, cadmium cations were incorporated into the hexagonal structure of ZnS and simultaneously oxygen atoms were replaced by sulfur atoms. Obviously, the diffraction peaks shifted toward the lower angle because of the enhancement in fringe lattice distance of the ZnS crystal structure due to the larger radius of Cd^{2+} than Zn^{2+} (0.97 and 0.74 Å, respectively). By further increase in Cd content, the peaks shifted to even lower angle and its crystal structure transferred from hexagonal ZnS to hexagonal wurtzite CdS (JCPDS No. 00-041-1049).
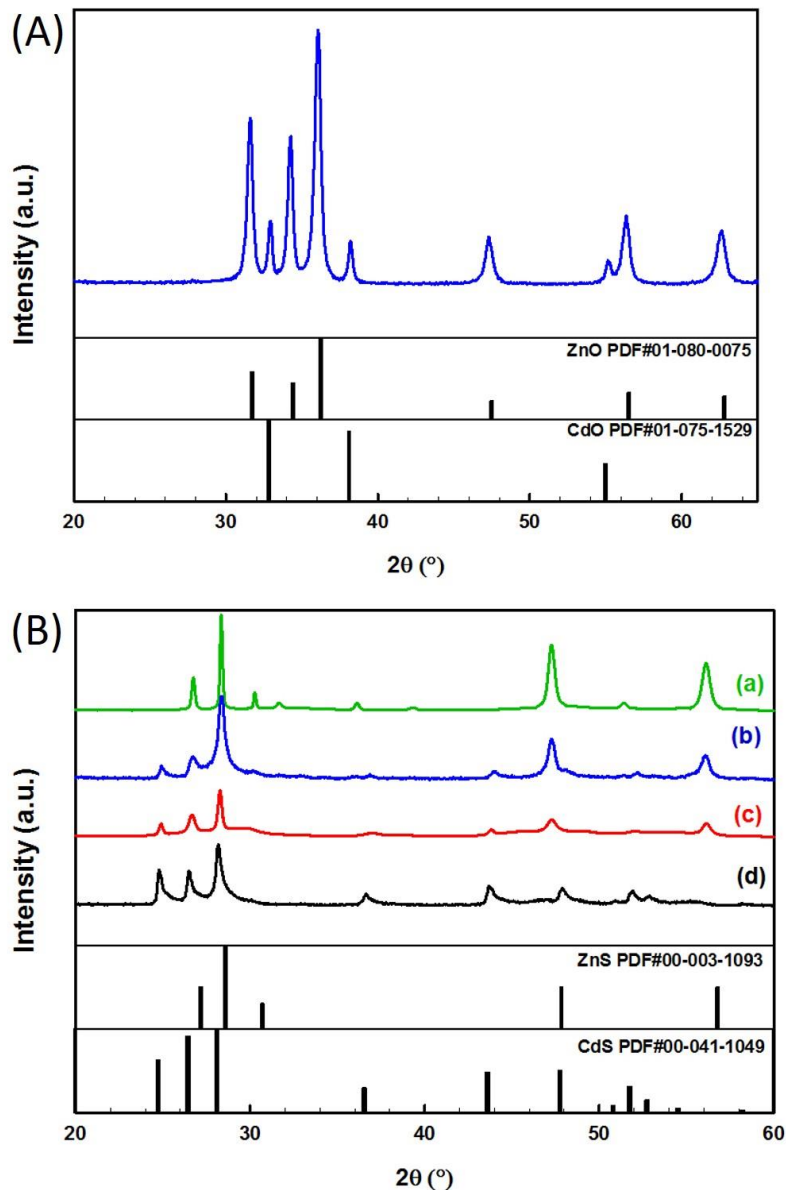
Figure 6.1. XRD patterns of (A) $Zn_{0.5}Cd_{0.5}O$ mixed oxide after calcination in air (B) solid solutions of (a) $Zn_{0.9}Cd_{0.1}S$ (b) $Zn_{0.7}Cd_{0.30}S$ (c) $Zn_{0.5}Cd_{0.5}S$ (d) $Zn_{0.3}Cd_{0.7}S$

According to XRD results, the two phases of ZnO and CdO were observed in $Zn_{0.5}Cd_{0.5}O$ after calcination (Figure 6.2-right). This mixed oxide doesn't have a clear band gap structure in visible region (Figure 6.2-left) and so it cannot generate excited charge carriers. Nevertheless, all solid solutions of $Zn_{1-x}Cd_xS$ exhibited clear band gap structure that can be excited in the visible region. It should be mentioned that ZnS can only be activated under UV light illumination because

of its large band gap (3.4 eV). Furthermore, by increasing the amount of Cd, the band gap decreases relatively and so the solid solutions could absorb more visible light energy. The lowest bandgap energy was related to CdS with 2.37 eV as it can be seen in Figure 6.2.
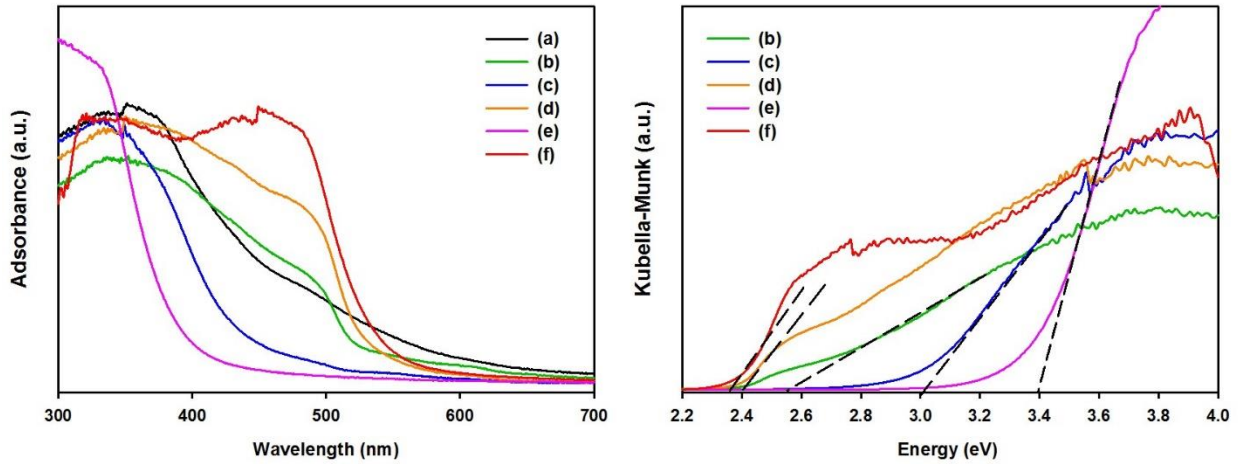

Figure 6.2. UV-Visible spectra and bandgap calculations of (a) $Zn_{0.50}Cd_{0.5}O$ (b) $Zn_{0.5}Cd_{0.5}S$ (c) $Zn_{0.7}Cd_{0.3}O$ (d) $Zn_{0.3}Cd_{0.7}O$ (e) ZnS (f) CdS
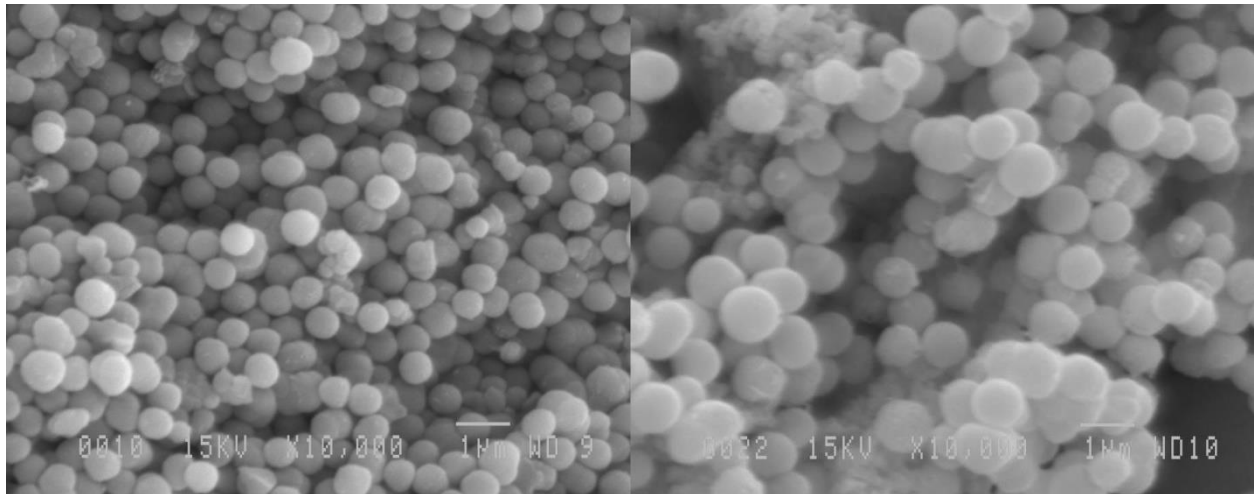

Figure 6.3. SEM images of ZnCd-glycerate after synthesized in an autoclave.

During the solvothermal step, metal-glycerate microspheres (ZnCd-glycerate) were formed in the autoclaves with a help of glycerol and metal cations.[364, 365] These microspheres were uniform with an average diameter of 500 nm, as shown in Figure 6.3. The metal-glycerate spheres were easily reacted with oxygen in air during calcination step and converted into a mixture of zinc

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and cadmium oxides. Interestingly, some carbon atoms remained in the mixture that will be discussed in detail in XPS section.

The morphology and 2D microstructure of $Zn_{0.5}Cd_{0.5}S$ solid solution are exhibited via TEM images in Figure 6.4. It is obvious that even after calcination and sulfuration steps, most of the microsphere structures were still preserved resulting from burning off carbon templates during calcination step (Figure 6.4-A, B). Clearly, these hollow spheres were mainly composed of well-defined nanoparticles in the range of 20 nm to 100 nm (Figure 6.4-C, D, E). Figure 6.4-F reveals the selected area election diffraction (SAED) pattern of an individual particle shown in Figure 6.4-G. The ring patterns can be attributed to (111), (220) and (311) planes of $Zn_{0.5}Cd_{0.5}Z$ with d-spacing of 0.32 nm, 0.19 nm, and 0.16 nm, respectively. Furthermore, high-resolution transmission electron microscope (HRTEM) perfectly shows the lattice structure of a typical nanoparticle. As it can be seen from Figure 6.4-H, the measurement shows that the interplanar spacing is 0.32 nm that corresponding to the interplanar distance of the (111) plane of $Zn_{0.5}Cd_{0.5}Z$.[363]

According to XPS characterizations that are illustrated in Figure 6.5, Zn 2p showed two different peaks at 1044.9 and 1021.7 (eV) which are related to Zn $2p_{1/2}$ and Zn $2P_{2/3}$, respectively. These binding energies confirmed that the valence state of zinc in the solid solution of $Zn_xCd_{1-x}S$ and ZnS were the same. Furthermore, there are two various peaks of Cd which can be attributed to Cd $3d_{3/2}$ at 412.0 (eV) and Cd $3d_{5/2}$ at 405.2 (eV). In addition, the whole S 2p spectrum can be deconvoluted into two main peaks for S $2P_{1/2}$ and S $2p_{3/2}$ at 163.1 and 161.9 (eV), respectively. These binding energies of Zn, Cd and S are in good agreement with CdS and ZnS which are reported in the literature.[87, 353, 354, 366] Interestingly, some carbon peaks were found in the XPS spectra of all samples. Although the samples were calcined at 500ºC for 4 hr, some carbon residues were not able to react with oxygen and left the sample. The spectrum of C 1s can be deconvoluted into 3 main peaks of 285, 286.7 and 289 (eV), that can be related to C-C, C-O and C=O chemical bonds, respectively (Figure 6.5-D).
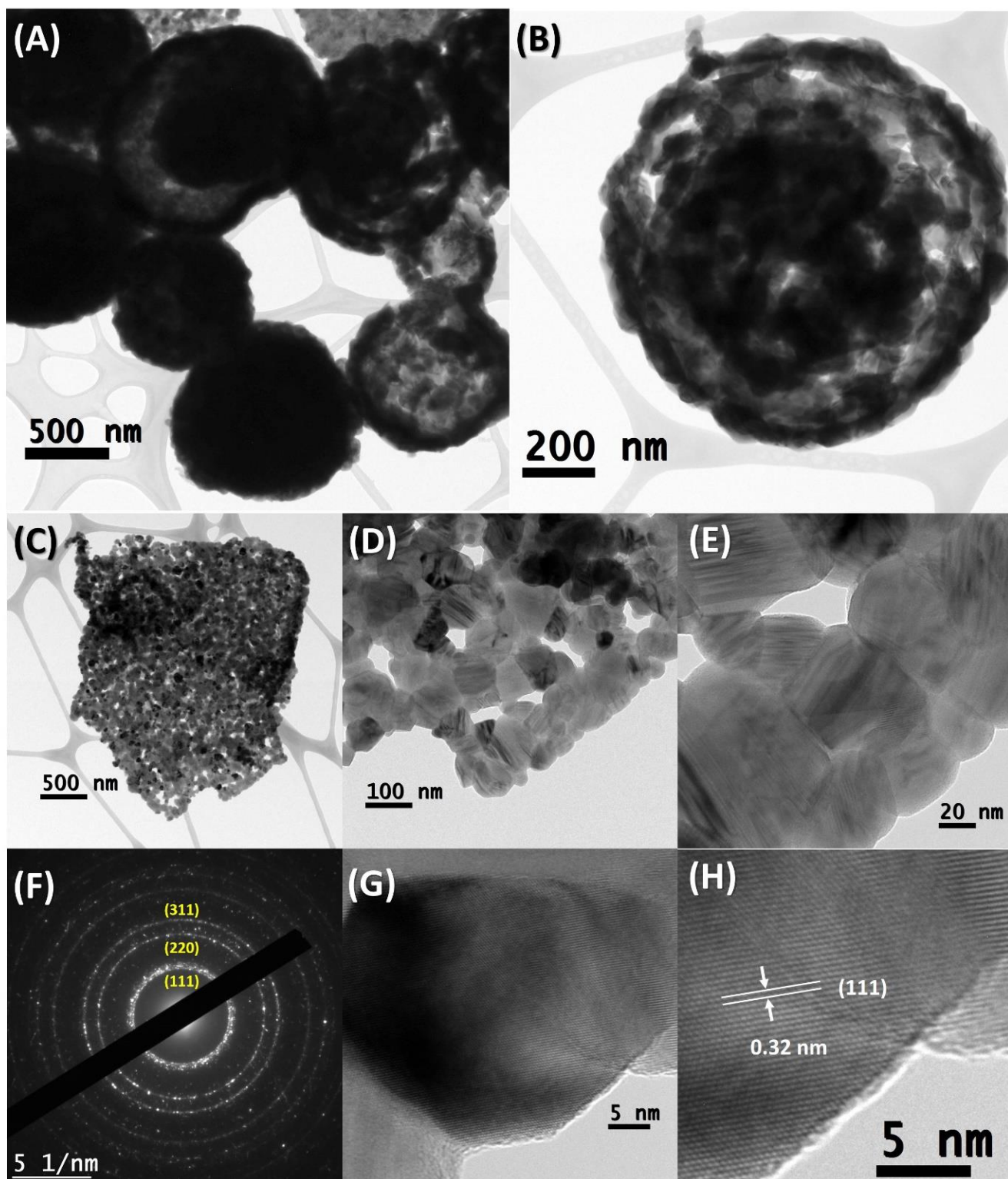
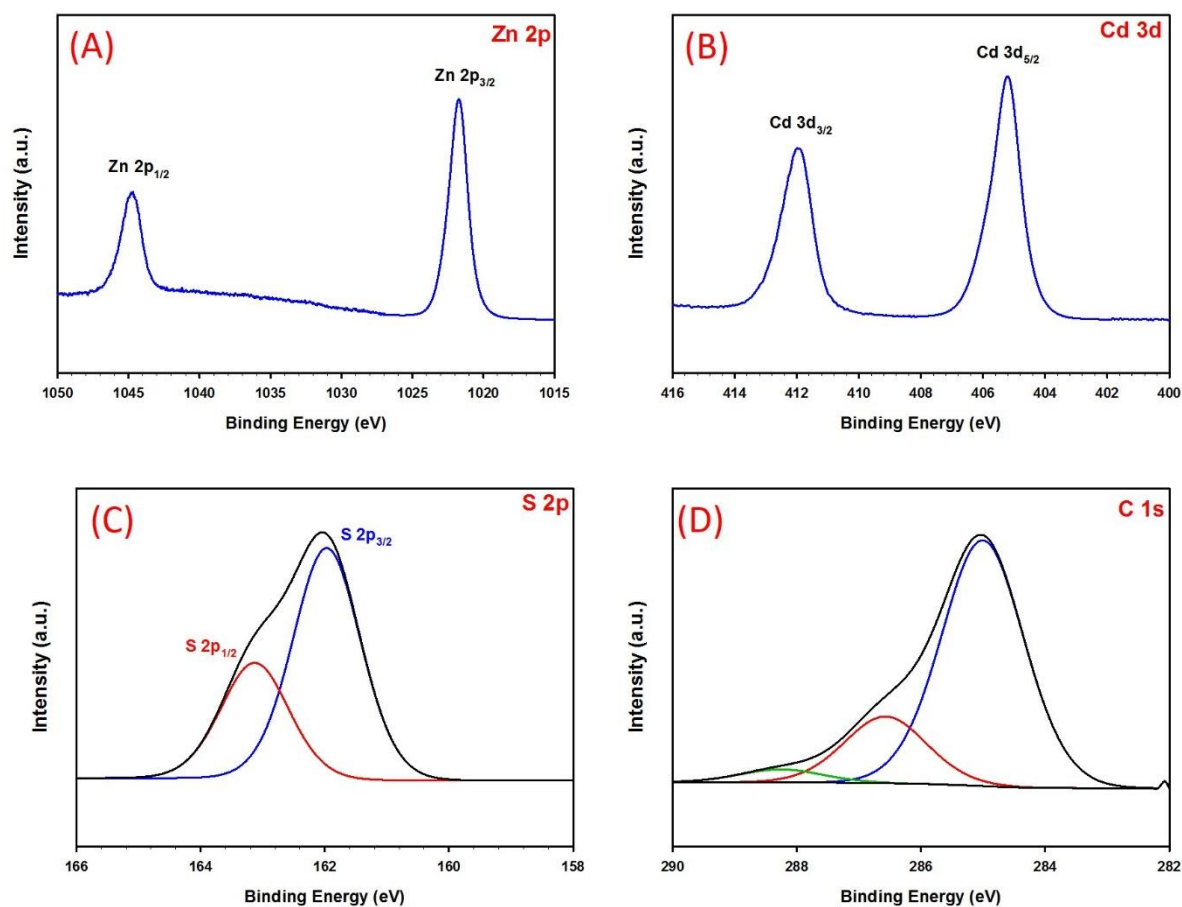Figure 6.4. (A-E) TEM images, (F) SAED pattern and (G,H) HRTEM of $Zn_{0.5}Cd_{0.5}S$ after H_2S treatment.

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Figure 6.5. XPS spectra of (A) Zn 2p, (B) Cd 3d, (C) S 2p and (D) C 1s of $Zn_{0.3}Cd_{0.7}S$

6.3.2 Photocatalytic hydrogen production

Hydrogen production of $Zn_xCd_{1-x}S$ in various conditions and different cocatalysts under solar simulator are displayed in Figure 6.6. It should be mentioned that in order to be able to compare results to each other most of the parameters including the amount of photocatalyst, sacrificial reagent and water were kept the same in all reactions. One of the most important parts of photocatalysis process is an optimum amount of cocatalyst because little amount of cocatalyst cannot produce enough active sites for reduction reactions and too much of it can cause to reduce light absorption on the photocatalyst surface which results in lower hydrogen generation. The best hydrogen production of the solid solution of $Zn_xCd_{1-x}S$ was achieved with using 2 wt% of Pt. This optimum amount of cocatalyst is the same in various concentration of Zn and Cd. Interestingly, MoS_2 also could be deposited on the surface of $Zn_xCd_{1-x}S$ via photo-deposition method and the

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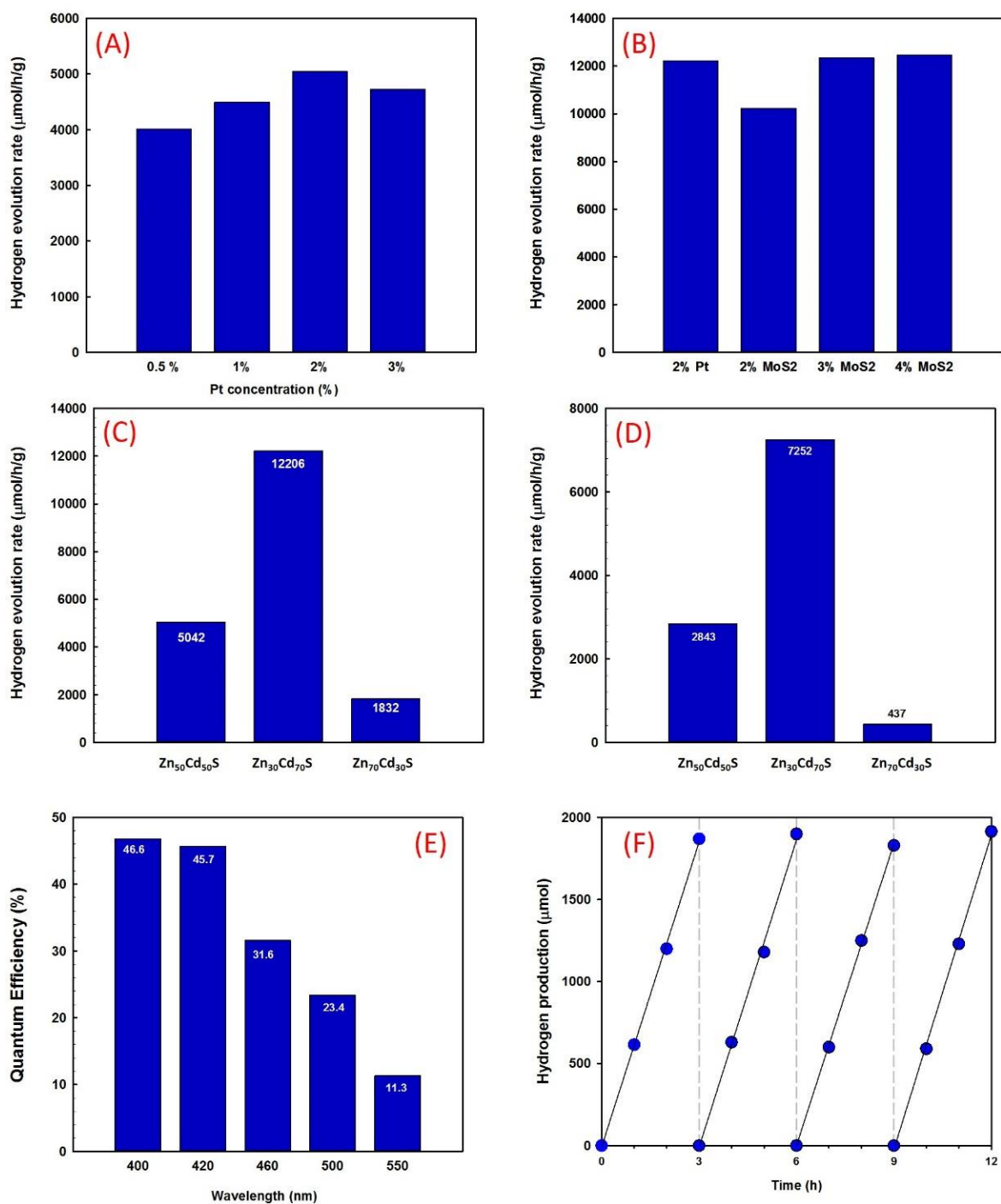
Figure 6.6. Hydrogen production of (A) $Zn_xCd_{1-x}S$ with various concentration of Pt as a cocatalyst under visible light (λ>420 nm), (B) 2% of Pt and different concentration of MoS_2 as cocatalysts deposited via photodeposited on $Zn_{0.3}Cd_{0.7}S$ (full spectrum), (C) various concentration of Zn and Cd in a solid solution of $Zn_xCd_{1-x}S$ under solar simulator full spectrum and (D) under visible light (λ>420 nm) with 3% MoS_2 as a cocatalyst. (E) Quantum efficiency of $Zn_{0.3}Cd_{0.7}S$ in various wavelengths under solar simulator irradiations via 3% MoS_2 as a cocatalyst. (F) Hydrogen production of $Zn_{0.3}Cd_{0.7}S$ for 4 cycles. Reaction Conditions: 50 mg of photocatalyst was dispersed in 100 ml aqueous solution of 0.5M Na_2S and Na_2SO_3.

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optimum amount of this cocatalyst was 3 wt% that could produce as much hydrogen as platinum in the same photocatalytic reaction conditions (Figure 6.6-B). It should be mentioned that using MoS_2 as a cocatalyst has some privileges in comparison with platinum because of its low cost and wide availability compared to platinum. Moreover, MoS_2 can be synthesized and deposited on various semiconductors via different approaches that would lead to developing more practical and efficient photocatalysts.

The observed high activity of MoS_2 can be attributed to physical and electrochemical properties of molybdenum and MoS_2. Firstly, Mo has smaller electronegativity than Pt (Pauling scale: 2.16 and 2.28, respectively).[367-369] Moreover, MoS_2 is a semiconductor with a direct band gap of 1.68 eV, which consists of the conduction band of Mo metal and valence band of S species.[370] The small band gap of MoS_2 helps that the excited charge carriers have a longer lifetime before recombination with together. In addition, the similarity of valence bands of MoS_2 and $Zn_xCd_{1-x}S$ leads to having the better-excited charge flow between the cocatalyst and the support. Furthermore, the work function of MoS_2 (5.15-5.39 eV) is slightly lower than Pt (5.22-5.60 eV) and so both cocatalysts showed similar performance for hydrogen generation.[370, 371]

Figure 6.6-C exhibits hydrogen generation of various concentration of $Zn_xCd_{1-x}S$ solid solutions under full spectrum illumination of solar simulator after 3 hr. Clearly, the highest amount of hydrogen produced with the $Zn_{0.3}Cd_{0.7}S$ solid solution which was around 12.206 mmol $h^{-1}gr^{-1}$. Moreover, this photocatalyst could produce more than 7.2 mmol h^{-1} gr^{-1} of hydrogen when a light filter ($\lambda \geq 420$ nm) of visible light was used. This amount of hydrogen generation was significantly higher than other concentrations of Zn and Cd. The reason could be attributed to the good development of crystal structure of Zn and Cd in this solid solution and also narrower band gap of $Zn_{0.3}Cd_{0.7}S$ in comparison with other concentrations. Furthermore, the quantum efficiencies of the $Zn_{0.3}Cd_{0.7}S$ solid solution was calculated via the various bandpass filters. Quantum efficiency at 400 and 420 nm are almost the same due to the fact that this semiconductor can mostly excited in visible light region (46.6% and 45.7%, respectively). Interestingly, this solid solution is active at much longer wavelengths as can be seen in Figure 6.6-E. The longest wavelength that $Zn_{0.3}Cd_{0.7}S$ can produce hydrogen was 550 nm with a quantum efficiency of 11.3%. In comparison with literatures, all of the QEs in various wavelengths of $Zn_{0.3}Cd_{0.7}S$ with MoS_2, are among the highest QE that has been reported for this kind of material.

This such high activity of $Zn_{0.3}Cd_{0.7}S$ with MoS_2 as a cocatalyst in a wide range of visible light spectrum can be explained by the uniform creation of hexagonal solid solution of ZnS and CdS. In addition, oxygen replacement by S_2^{-2} during sulfuration led to having some defects on the surface of the solid photocatalyst, which could be acted as excited charges pools.[270, 372] These pools can help to deposit cocatalyst much easier and they can also help to produce hydrogen more efficiently.

6.4 Conclusion

The zinc cadmium sulfide ($Zn_xCd_{1-x}S$) solid solution is one of the best semiconductors can act as a photocatalyst to generate hydrogen from water under sunlight illumination. Its crystal structure as a solid solution can be controlled by varying different amount of Zn/Cd ratio. Therefore, this solid solution possesses an adjustable conduction and valence bands positions as well as controllable band gap. In addition, its considerably stronger stability in comparison with CdS alone during photocatalytic reactions, make it a good candidate for the further industrial application. In this work, metal-glycerate from zinc and cadmium was synthesized via the solvothermal method. Then, the mixture of mixed oxides of ZnO and CdO was created from the metal-glycerate. After this step, sulfide ions (S^{-2}) was used in order to convert mixed oxides into solid solution of $Zn_xCd_{1-x}S$. The obtained semiconductor can absorb a wide range of visible light energy because of its narrow band gap. The best results for hydrogen production from water splitting reaction were obtained by utilizing Zn/Cd = 0.3/0.7. Interestingly, utilizing MoS_2 as a cocatalyst could generate almost the same amount of hydrogen as Pt which was around 12 mmol h^{-1} g^{-1} hydrogen under solar simulator illumination. Moreover, the calculated quantum efficiencies were 46.6% at 400 nm, 23.4% at 500 nm and 11.3% at 550 nm, which were among the highest quantum efficiencies have ever reported for this semiconductor.