AuPd bimetallic nanoparticles decorated Cd_{0.5}Zn_{0.5}S photocatalysts with enhanced visible-light photocatalytic H₂ production activity

Linen Wu^{a, b}, Jie Gong^b, Lei Ge^{* a, b}, Changcun Han^b, Siman Fang^b,

Yongji Xin^b, Yujing Li^b, Yan Lu^b

^a State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum Beijing, No. 18 Fuxue Rd., Beijing 102249, People's Republic of China.

^b Department of Materials Science and Engineering, College of Science, China University of Petroleum Beijing, No. 18 Fuxue Rd., Beijing 102249, People's Republic of China.

Abstract:

In this study, novel AuPd bimetallic co-catalyst decorated Cd_{0.5}Zn_{0.5}S photocatalyst was successfully synthesized via an in-situ chemical deposition method. The physical as well as the photophysical properties of the as-obtained AuPd/Cd_{0.5}Zn_{0.5}S samples were characterized by X-ray diffractometry (XRD), Transmission electron microscope (TEM), UV-vis diffusion reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS) and surface photovoltage spectroscopy (SPV). The AuPd bimetallic co-catalysts showed dramatic photo-generated charge separation efficiency in Cd_{0.5}Zn_{0.5}S sample, and thus significantly enhance the H₂ production activity under visible light irradiation. The AuPd/Cd_{0.5}Zn_{0.5}S sample with 0.5 wt% content had the highest catalytic activity, and the corresponding H₂ evolution rate is 3.65 mmol·g⁻¹·h⁻¹, which was about 12 times as that of pure Cd_{0.5}Zn_{0.5}S sample under visible light irradiation. The photocatalytic activity of the photocatalyst was stable even after 9 cycling photocatalytic experiments. A possible mechanism on the photocatalytic enhancement of AuPd NPs was systematically investigated, which can provide a novel concept for the synthesis of other desirable photocatalytic materials.

Keywords: Cd_{0.5}Zn_{0.5}S; Photocatalyst; AuPd bimetallic alloy; Water splitting; Visible light.

* Corresponding author at: State Key Laboratory of Heavy Oil Processing, China University of Petroleum Beijing, No. 18 Fuxue Road,

Beijing 102249, PR China. Tel/Fax.: +86 1089739096. E-mail address: gelei08@sina.com (L.Ge)

1. Introduction

Due to rapid industrial growth and population, the energy crisis and environmental pollution are becoming major issues which need to be addressed worldwide. As a promising approach for new energy sources, photocatalytic hydrogen production from water splitting under solar light irradiation is a sustainable strategy.¹⁻³ Since Honda and Fujishima discovered the photocatalytic water splitting on TiO_2 electrodes in 1972,⁴ several investigations are focused on semiconductors such as oxides, oxynitrides, and metal sulfides in H_2 evolution by water splitting under solar radiation.⁵⁻¹¹ However, some semiconductors with large bandgap such as TiO_2 and ZnO could only respond to photons with wavelength in UV range which absorbs only about 4% of solar energy; and limit their application to a great extent.¹²⁻¹⁴ Therefore, the development of simple, efficient and renewable visible photocatalysts is a major challenge in this field.

Recently, metal sulfide semiconductors have been received considerable attention in photocatalytic H_2 production due to their appropriate bandgap and catalytic function.¹⁵⁻¹⁹ Among them, cadmium sulfide (CdS) with a band gap of ~ 2.49 eV has gained intensive attention. However, its relatively rapid recombination kinetics of the excited electron-hole pairs and photocorrosion result in low quantum efficiencies and limit its photocatalytic efficiency. To enhance its photocatalytic activity, constructing ternary metal sulfide solid solution such as $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ is a viable method. It is reported that $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ is a good candidate in H_2 production under visible light.²⁰⁻²¹ More importantly, it exhibits better performance than CdS and ZnS . That means, the new energy band will respond to visible light and can generate hydrogen more efficient than CdS does. Although the photocatalytic activities of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ have been investigated, it still suffers from fast recombination of charge carriers. Therefore, it is necessary to further improve photocatalytic activity of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. Various attempts have been made to enhance the photocatalytic performance of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$, such as bismuth-doping,²² graphene-based (RGO)- $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ composites,²³⁻²⁴ semiconductor synergic effect.²⁵⁻²⁷ Among various

strategies, the rapid separation-transfer-transformation of photo-generated charge carriers is a key issue, which should be emphatically addressed.

It has been indicated that the decoration of semiconductor particles with monometallic NPs may effectively capture photo-generated electrons, which potentially prolongs the lifetime of active radicals and may achieve more efficient H₂ production activity.²⁸⁻³³ It is observed that the selectivity, activity and resistance to poisoning of the metal catalysts can be drastically influenced by the presence of a second metal component. Multifarious bimetallic alloy NPs, such as AuPt,³⁴ PtNi,³⁵ AuCu³⁶ and PtSn³⁷ has been studied extensively. Among them, AuPd bimetallic nanoparticles have been proven to be an ideal candidate for co-catalyst in various catalytic reactions.³⁸⁻⁴¹ Very recently, our group has found that the AuPd bimetallic NPs decorated g-C₃N₄ photocatalysts and TiO₂ nanosheets showed significantly enhance H₂ evolution activity.⁴²⁻⁴³ Despite these success reports, the study on AuPd bimetallic NPs for photocatalytic water splitting has still been limited. Therefore, it should be of interest to explore AuPd bimetallic NPs decorated photocatalysts which conspicuously enhance the catalytic activities.

In this study, for the first time we report the synthesis of AuPd/Cd_{0.5}Zn_{0.5}S photocatalyst via an in-situ synthesis method. The photocatalytic activity of Cd_{0.5}Zn_{0.5}S can be significantly enhanced by introducing the mono-dispersed AuPd bimetallic NPs. The 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample shows the highest H₂ production activity of 3.65 mmol·h⁻¹·g⁻¹, which is about 12 times as that of pure Cd_{0.5}Zn_{0.5}S under the same conditions. The effects of AuPd alloy NPs contents on the charge transfer process and photocatalytic activity were investigated in detail; and the photocatalytic mechanism for enhanced H₂ evolution activity was also proposed. The work may provide more insight into synthesizing novel hybrid photocatalytic materials with high efficiency in energy and environmental applications.

Experimental

2.1. Materials

HAuCl₄·3H₂O (1.0 g, A.R.), PdCl₂ (1.0 g, A.R.), poly vinyl alcohol (PVA, Aldrich, M_w=10 000,

80% hydrolyzed), sodium carbonate (A.R), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2$, Aladdin), cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, Aladdin, 98%) and NaBH_4 (Aladdin, 98%) were used as received without additional purification or treatment. Distilled water was used in all experiments.

2.2 Synthesis of the photocatalysts

The $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ samples were prepared according to a literature method with a slight modification.⁴⁴ Sodium thiobenzoate was prepared by allowing 2.86 g sodium carbonate and 3.04 g thiobenzoic acid to react in water at room temperature. The obtained sodium thiobenzoate was added to 5 mM cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) and 5 mM zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) mixing aqueous solutions under stirring, then the products were transferred into a 100 mL capacity Teflon-lined stainless steel autoclave, and heated at 140 °C for 3 h. The final product was washed with deionized water and ethanol for three times respectively by centrifugation, and dried at 60 °C for 8 h.

The preparation of $\text{AuPd}/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ composite photocatalysts is described as follows:⁴⁵ 1 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and PdCl_2 aqueous solution were first prepared. Fresh aqueous solutions of 0.1 M NaBH_4 and PVA were also prepared in advance. In a typical procedure, 0.1 g as-prepared $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ was dispersed into a beaker containing 50 ml deionized water, and sonicated for 30 min. The PdCl_2 and HAuCl_4 stock solution were mixed in the desired ratio and the required amount (1.0 wt%) of a PVA solution was added dropwise ($\text{PVA}/(\text{Au}+\text{Pd})=1.2$, weight ratio) into the as-prepared $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ aqueous solution, the fresh NaBH_4 solution ($\text{NaBH}_4/(\text{Au} + \text{Pd}) = 5$, molar ratio) was then added to form a dark-yellow solution and stirred for 120 min. The final product was washed with deionized water and ethanol for three times respectively by centrifugation, and then dried in a vacuum oven at 60 °C for 12 h. Then, $\text{AuPd}/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ with different amounts of AuPd bimetallic NPs was obtained. The weight percentages of AuPd in the initial photocatalyst precursors were 0.1 wt%, 0.3 wt%, 0.5 wt%, 1.0 wt% and 2.0 wt%, respectively. For comparison, 0.5 wt% $\text{Au}/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ and 0.5 wt% $\text{Pd}/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ were also prepared.

2.3. Characterization

The crystal phases of the samples were investigated via X-ray diffraction (XRD; Bruker D8 Advance) with Cu K α radiation at a scan rate of 4 min⁻¹. The microstructures of the samples were analyzed by transmission electron microscopy (TEM, JEM-2100, accelerating voltage 200 kV). UV-vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-4100 spectrophotometer using BaSO₄ as the reference material. The X-ray photoelectron spectroscopy (XPS) was measured in a PHI 5300 ESCA system. The beam voltage was 3.0 eV, and the energy of Ar ion beam was 1.0 keV. All the binding energies were referenced to the signal for adventitious carbon at 284.8 eV.

2.4. Photocatalytic activity

The photocatalytic H₂ evolution experiments were performed in Perfectlight Labsolar IIAG system with a 300 ml quartz reactor at 4 °C. The reactor is connected to a low-temperature thermostat bath. PLS-SXE 300UV Xe arc lamp through a UV-cutoff (≥ 400 nm) filter was used as the visible light source. The light intensity employed was 35 mW/cm². In a typical photocatalytic H₂ production experiment, 50 mg of catalyst was dispersed with a constant stirring in 80 ml of mixed aqueous solution containing 0.44 M Na₂S and 0.31 M Na₂SO₃. Before photocatalytic experiments, the reaction vessel was evacuated for 30 min to remove the dissolved oxygen to ensure that the vacuum conditions. The products were analyzed by gas chromatography (Beifen 3420A), with high purity Argon as a carrier gas and equipped with a thermal conductivity detector.

2.5. SPV measurements

The surface photovoltage (SPV) measurement was carried out on a surface photovoltage spectroscopy (PL-SPS/IPCE1000 Beijing Perfect Light Technology Co., Ltd). The measurement system consists of a source of monochromatic light, a locking amplifier (SR830, Stanford research systems, Inc.) with a light chopper (SR 540, Stanford research systems, Inc.), and a sample chamber. The monochromatic light is provided by passing light from a 500 W xenon lamp (CHFXQ500 W,

global xenon lamp power) through a grating mono-chromator (Omni-5007, No.09010, Zolix), which chopped with a frequency of 24 Hz. All the measurements were operated under ambient pressure at room temperature.

3. Results and discussion

3.1. Characterization of Au-Pd/Cd_{0.5}Zn_{0.5}S composite samples

The XRD patterns of as-prepared AuPd/Cd_{0.5}Zn_{0.5}S photocatalysts are depicted in Fig.1. Typical diffraction peaks corresponding to CdS ($2\theta = 26.83^\circ, 30.6^\circ, 44.83^\circ, 53.05^\circ$) and ZnS ($2\theta = 28.58^\circ, 47.5^\circ$) are observed in all the samples, which are in good agreement with the phase of CdS in JCPDS No.65-8837 and ZnS in JCPDS No.65-9585, respectively. It is obvious that the doping of bimetallic AuPd species wouldn't affect the crystal structure of Cd_{0.5}Zn_{0.5}S photocatalysts. However, no apparent diffraction peaks of AuPd NPs were observed in all the samples. The results indicate that the bimetallic AuPd depositing content in sample Au-Pd/Cd_{0.5}Zn_{0.5}S is too low to be detected by XRD. Nevertheless, the presence of AuPd bimetallic alloys in the composites can be easily evidenced by TEM and XPS techniques as discussed later.

TEM was further applied to investigate the microstructures of Cd_{0.5}Zn_{0.5}S and AuPd/Cd_{0.5}Zn_{0.5}S composite samples. As shown in Fig. 2 (a), it can be seen that the Cd_{0.5}Zn_{0.5}S are composed of a large quantity of mono-dispersed spheres with diameter of 150 nm~ 200 nm. An interesting feature is that each sphere consists of an agglomeration of several crystallites. Fig. 2 (b and c) illustrates TEM image for the AuPd/Cd_{0.5}Zn_{0.5}S photocatalyst. After the chemical reduction deposition of AuPd species on Cd_{0.5}Zn_{0.5}S, the AuPd bimetallic species was deposited as nanoparticles on the Cd_{0.5}Zn_{0.5}S surface with high dispersion, and there is no obvious change in the microstructure of Cd_{0.5}Zn_{0.5}S spheres. Fig. 2 (d) presents the HRTEM image of the AuPd/Cd_{0.5}Zn_{0.5}S composite, where AuPd NPs can be seen as having certain orientations and lattice spacings. The lattice spacing of 0.244 nm can be ascribed to the AuPd alloys.⁴² In addition, the identified lattice fringes of ~0.313 nm corresponds to the (101) lattice plane of

Cd_{0.5}Zn_{0.5}S phase.¹⁶ The TEM results indicate that the intimate interfaces are formed between AuPd and Cd_{0.5}Zn_{0.5}S, which can improve the separation efficiency of photo-generated electrons-holes.

UV-Vis diffuse reflectance spectroscopy (DRS) was performed to justify the light-harvesting ability of the as-prepared AuPd/Cd_{0.5}Zn_{0.5}S composite samples. As shown in Fig. 3, the pure Cd_{0.5}Zn_{0.5}S sample show absorption from the UV through the visible range with the steep shape spectrum, indicating that the visible light absorption is ascribed to the band gap transition.⁴² After introducing AuPd bimetallic NPs, the AuPd/Cd_{0.5}Zn_{0.5}S samples show the similar absorption edge in shape and exhibit significantly enhanced light absorption intensity compared with the pure Cd_{0.5}Zn_{0.5}S in the visible region. The absorption intensity of the as-prepared samples strengthen with increasing AuPd NPs contents, which agrees with the color of the prepared samples that vary from light yellow to dark gray. The DRS results further confirm that the chemical in-situ deposited AuPd bimetallic NPs has considerable importance to the efficient utilization of visible light, and hence is expected to have superior photocatalytic performance.

X-ray photoelectron spectroscopy (XPS) analysis was explored in order to gain deeper insight into the surface deposition of AuPd/Cd_{0.5}Zn_{0.5}S sample. Fig. 4 (f) presents the survey spectrum of the AuPd/Cd_{0.5}Zn_{0.5}S sample, which confirms the coexistence of Zn, Cd, S, Au and Pd elements as expected. In the Zn 2p and Cd 3d XPS spectras (Fig 4a and b), the binding energies of Zn 2p (1021.6 ev and 1044.7 ev) and Cd 3d (404.6 ev and 411.4 ev) agree well with the values reported in other work.⁴⁶ The S 2p XPS binding energy can be deconvoluted into three peaks located at 161.1, 161.5 and 162.4 eV, which are assigned to the S²⁻ state.⁴⁷ As shown in Fig. 4d, the Pd 3d spectra of AuPd/Cd_{0.5}Zn_{0.5}S could be fitted into asymmetric peaks, suggesting the existence of two states of Pd species. The Pd 3d_{5/2} peak at 335.03eV and Pd 3d_{3/2} peak at 340.1 eV are attributed to the metallic Pd⁰, where the binding energy peaks shown at 335.83 eV is originated form of Pd²⁺, respectively.⁴⁸ Furthermore, the Au 4f_{7/2} and Au 4f_{5/2} peaks locate at 83.1 and 88.5 eV respectively in the spectrum of

AuPd/Cd_{0.5}Zn_{0.5}S, which exhibit slight downshift as compared to that of Au/TiO₂.⁴⁹ The shift of binding energy for Au in the AuPd/Cd_{0.5}Zn_{0.5}S samples may be ascribed to the charge transfer due to the formation of AuPd bimetallic alloy.⁴³

3.2. Photocatalytic H₂ evolution activity

The photocatalytic activities of the AuPd/Cd_{0.5}Zn_{0.5}S composite photocatalysts were evaluated by H₂ evolution from an aqueous solution containing 0.44 M Na₂S and 0.31 M Na₂SO₃ under visible light irradiation. As shown in Fig. 5, the pure Cd_{0.5}Zn_{0.5}S sample without AuPd loading shows photocatalytic H₂ production activity of 0.4 mmol·g⁻¹·h⁻¹. After introducing of AuPd NPs, the photocatalytic H₂ evolution activity is significantly enhanced. Fig. 6 presents the H₂ evolution rate over AuPd/Cd_{0.5}Zn_{0.5}S composite samples with different AuPd contents. After loading 0.1 wt% AuPd NPs on the Cd_{0.5}Zn_{0.5}S sphere, the H₂ evolution activity is remarkably increased to 1.328 mmol·g⁻¹·h⁻¹. Along with the increase of the AuPd NPs amounts, the H₂ evolution is further improved. The 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample shows the highest H₂ evolution rate of 3.65 mmol·g⁻¹·h⁻¹, which is 12 times higher than that of pure Cd_{0.5}Zn_{0.5}S. The enhanced photocatalytic performance may be attributed to the intimate interfaces between AuPd and Cd_{0.5}Zn_{0.5}S, which can effectively promote the separation efficiency of the photo-generated electron-hole pairs. However, a further increase of AuPd content leads to a decrease of H₂ evolution. The decrease in the photocatalytic activity may be due to the high ratio of black AuPd NPs, which can lead to shielding of the active sites on the photocatalyst surface thus reduce quantum efficiency. Therefore, a suitable content of AuPd NPs is important for optimizing the photocatalytic activity of AuPd/Cd_{0.5}Zn_{0.5}S samples.

In order to further demonstrate the role of AuPd alloy in the photocatalytic process, the photocatalytic activities of Au/Cd_{0.5}Zn_{0.5}S and Pd/Cd_{0.5}Zn_{0.5}S samples were conducted for comparison. As shown in Fig. 5 and 6, after loading Au and Pd on Cd_{0.5}Zn_{0.5}S nanoparticles, the catalytic H₂ production were also obviously improved. The 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample shows the highest

photocatalytic performance, which is about 9.1 and 2.5 times higher than 0.5 wt% Au/Cd_{0.5}Zn_{0.5}S and 0.5 wt% Pd/Cd_{0.5}Zn_{0.5}S samples. The results indicate that the AuPd bimetallic NPs play an important role in the enhancement of H₂ evolution activity in the AuPd/Cd_{0.5}Zn_{0.5}S composite photocatalysts. For comparison, the photocatalytic activity of mechanical mixture 0.5 wt% (Au+Pd)/Cd_{0.5}Zn_{0.5}S was also examined in the same system under the same condition, and the sample only had an activity of 1.217 mmol•h⁻¹•g⁻¹ which was much lower than 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S.

The stability of a photocatalyst is important for its practical applications. The catalytic stability of the 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample was further investigated via cycling experiments of photocatalytic H₂ evolution. Fig. 7 shows the H₂ evolution curves in cycling photocatalytic run. The H₂ production does not display obvious decrease after irradiated for 36 h (9 cycles), which indicates that the AuPd/Cd_{0.5}Zn_{0.5}S photocatalyst has sufficient stability for photocatalytic H₂ production.

3.3. Photocatalytic mechanism investigation

Based on the structure characterizations and the visible light photocatalytic performance of AuPd/Cd_{0.5}Zn_{0.5}S, a possible mechanism for photocatalytic H₂ evolution over the AuPd/Cd_{0.5}Zn_{0.5}S catalyst is proposed. As illustrated in Fig. 8 (a, b), Cd_{0.5}Zn_{0.5}S absorbs photons and excites electron-hole pairs under visible-light irradiation. However, without the co-catalyst, the photo-generated electrons and holes are likely to recombine rapidly resulting in a low photocatalytic H₂ production activity. However, after introducing AuPd NPs, AuPd NPs show higher electron-capture capability and can stimulate photo-generated electrons transfer from Cd_{0.5}Zn_{0.5}S towards AuPd NPs surface due to their lower Fermi level, leading to efficient separation of the hole-electron pairs. The AuPd alloys can act as an electron collector and transporter to prolong the lifetime of the charge carriers, thus improving the photocatalytic activity.⁴²⁻⁴³ In addition, the AuPd NPs and Cd_{0.5}Zn_{0.5}S can closely bound together and form interfaces, which can offer a larger active surface area and maximize the electrons transfer efficiency. The holes in the VB of Cd_{0.5}Zn_{0.5}S are consumed by Na₂S and Na₂SO₃

sacrificial reagents. As a consequence, the recombination process of the electron-hole pairs is effectively inhibited, resulting in obviously improvement of H₂ production activity for the AuPd/Cd_{0.5}Zn_{0.5}S photocatalyst. Different reactions occurred for the whole procedure can be represented as follows:

In order to confirm the above analysis, it is necessary and important to fully understand the behaviors of charge carriers in AuPd/Cd_{0.5}Zn_{0.5}S catalyst system.⁵⁰ The surface photovoltage spectroscopy (SPV) technique has become a powerful tool in studying the kinetic behaviors of the charge transfer process occurring in the as-prepared AuPd/Cd_{0.5}Zn_{0.5}S samples, which could be beneficial for fully understanding the effect of AuPd NPs. The SPV signal can identify the light-responsive wavelength range and the electrons-holes separation efficiency in the photocatalysts. Fig.9 illustrates the SPV spectra of AuPd/Cd_{0.5}Zn_{0.5}S with different AuPd bimetal contents. The SPV signal ranging from 300 to 550 nm is observed for pure Cd_{0.5}Zn_{0.5}S. The intensity of the SPV spectra represents the separation efficiency of photo-induced charge carriers. Compared to the pure Cd_{0.5}Zn_{0.5}S, the AuPd/Cd_{0.5}Zn_{0.5}S samples exhibit stronger SPV signal. The results indicate that the photo-generated electron-hole pairs are separated more effectively. Notably, the 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample shows the highest SPV signal intensity, indicating the maximal separating efficiency of electron-hole pairs. However, if excessive AuPd NPs are introduced, the light absorption by Cd_{0.5}Zn_{0.5}S is reduced as excess AuPd NPs prevent the light absorption from reaching the Cd_{0.5}Zn_{0.5}S surface, which leads to a

decrease of the SPV signal in comparison to that of the 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample. The phenomenon illustrates that an optimal content of bimetallic AuPd NPs is favorable for electron-hole separation in the AuPd/Cd_{0.5}Zn_{0.5}S system. Moreover, the SPV spectra are consistent with the results of photocatalytic H₂ evolution, which corresponds to an efficient charge separation in the AuPd/Cd_{0.5}Zn_{0.5}S composites.

2. Conclusions

In summary, the AuPd/Cd_{0.5}Zn_{0.5}S photocatalyst with significantly enhanced photocatalytic H₂ production activity under visible light irradiation was successfully synthesized. The photocatalytic activity was enhanced in the presence of AuPd NPs, and the highest efficiency was observed on 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S sample, which is 12 times higher than that of pure Cd_{0.5}Zn_{0.5}S. The presence of AuPd could increase the interfacial charge transfer and inhibit the recombination of electron-hole pairs. Finally, a possible photocatalytic mechanism is proposed based on the experimental results, which has been confirmed by the surface photovoltage (SPV) technique. Therefore, the results illustrate that the AuPd bimetallic NPs are a promising co-catalyst, which can be potentially used in photocatalytic H₂ production process.

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References

- [1] Zou ZG, Ye JH, Sayama K, Arakawa H. Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature* 2001; 414: 625-7.
- [2] Khan SUM, Al-Shahry M, Ingler WB. Efficient photochemical water splitting by a chemically modified n-TiO₂. *Science* 2002; 297: 2243-5.

- [3] Maeda K, Domen K. New non-oxide photocatalysts designed for overall water splitting under visible light. *J Phys Chem C* 2007; 111: 7851-61.
- [4] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972; 238: 37-8.
- [5] Kudo A, Miseki Y. Heterogeneous photocatalyst materials for water splitting. *Chem Soc Rev* 2009; 38: 253-78.
- [6] Navarro RM, Alvarez-Galvan MC, de la Mano JAV, AlZahrani SM, Fierro JLG. A framework for visible-light water splitting. *Energy Environ Sci* 2010; 3: 1865-82.
- [7] Johnson TC, Morris DJ, Wills M, Hydrogen generation from formic acid and alcohols using homogeneous catalysts. *Chem Soc Rev* 2010; 39: 81-8.
- [8] Ran JR, Yu JG, Jaroniec M. Ni(OH)₂ modified CdS nanorods for highly efficient visible-light-driven photocatalytic H₂ generation. *Green Chem* 2011; 13: 2708-13.
- [9] Qi LF, Yu JG, Jaroniec M. Preparation and enhanced visible-light photocatalytic H₂-production activity of CdS-sensitized Pt/TiO₂ nanosheets with exposed (001) facets. *Phys Chem Chem Phys* 2011; 13: 8915-23.
- [10] Wen JQ, Li X, Liu W, Fang YP, Xie J, Xu YH. Photocatalysis fundamentals and surface modification of TiO₂ nanomaterials. *Chinese. J. Catal* 2015; 36: 2049-70.
- [11] Wen JQ, Li X, Li HQ, Ma S, He KL, Xu YH, Fang YP, Liu W, Gao QZ. Enhanced visible-light H₂ evolution of g-C₃N₄ photocatalysts via the synergetic effect of amorphous NiS and cheap metal-free carbon black nanoparticles as co-catalysts. *Appl. Surf. Sci* 2015; 358: 204-12.
- [12] Girish Kumar S, Gomathi Devi L. Review on modified TiO₂ photocatalysis under UV/Visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics. *J Phys Chem A* 2011; 115: 13211-41.
- [13] Paramasivam I, Jha H, Liu N, Schmuki P. A review of photocatalysis using self-organized TiO₂

nanotubes and other ordered oxide nanostructures. *Small* 2012; 8: 3073-103.

[14] Park NG, van de Lagemaat G, Frank AJ. Comparison of dye-sensitized rutile- and anatase-based TiO_2 solar cells. *J Phys Chem B* 2000; 104: 8989-94.

[15] Reber JF, Rusek M. Photochemical hydrogen production with platinized suspensions of cadmium sulfide and cadmium zinc sulfide modified by silver sulfide. *J Phys Chem* 1986; 90: 824-34.

[16] Zhang J, Yu JG, Zhang YM, Li Q, Gong JR. Visible light photocatalytic H_2 -production activity of CuS/ZnS porous nanosheets based on photoinduced interfacial charge transfer. *Nano Lett* 2011; 11: 4774-9.

[17] Zhang J, Liu SW, Yu JG, Jaroniec M. A simple cation exchange approach to Bi-doped ZnS hollow spheres with enhanced UV and visible-light photocatalytic H_2 -production activity. *J Mater Chem* 2011; 21: 14655-62.

[18] Zhang J, Yu JG, Jaroniec M, Gong JR. Noble metal-free reduced graphene oxide- $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanocomposite with enhanced solar photocatalytic H_2 -production performance. *Nano Lett* 2012; 12: 4584-89.

[19] Li Q, Li X, Wageh S, Al-Ghamdi AA, Yu JG. CdS/Graphene nanocomposite photocatalysts. *Adv. Energy Mater* 2015; 5: 1500010.

[20] Zhang K, Jing DW, Xing CJ, Guo LJ. Significantly improved photocatalytic hydrogen production activity over $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ photocatalysts prepared by a novel thermal sulfuration method. *Int J Hydrogen Energy* 2007; 32: 4685-91.

[21] del Valle F, Ishikawa A, Domen K, Villoria de la Mano JA. Influence of Zn concentration in the activity of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions for water splitting under visible light. *Catal Today* 2009; 143: 51-6.

[22] Peng SQ, An R, Li YX, Lu GX, Li SB. Remarkable enhancement of photocatalytic hydrogen evolution over $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ by bismuth-doping. *Int. J. Hydrogen. Energ* 2012; 37: 1366-74.

- [23] Liu MC, Wang LZ, Lu GQ, Yao XD, Guo LJ. Twins in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solution: Highly efficient photocatalyst for hydrogen generation from water. *Energy Environ Sci* 2011; 4: 1372-78.
- [24] Zhang J, Zhao WW, Xu Y, Xu HL, Zhang B. In-situ photo-reducing graphene oxide to create $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ porous nanosheets/RGO composites as highly stable and efficient photoelectrocatalysts for visible-light-driven water splitting. *Int. J. Hydrogen. Energ* 2014; 39: 702-10.
- [25] Xie SL, Lu XH, Zhai T, Gan JY, Li W, Xu M, Yu MH, Zhang YM, Tong YX. Controllable synthesis of $\text{Zn}_x\text{Cd}_{1-x}\text{S}@\text{ZnO}$ core-shell nanorods with enhanced photocatalytic activity. *Langmuir* 2012; 28: 10558-64.
- [26] Wang XX, Chen J, Guan CJ, Guo LJ. Enhanced efficiency and stability for visible light driven water splitting hydrogen production over $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{g-C}_3\text{N}_4$ composite photocatalyst. *Int. J. Hydrogen. Energ* 2015; 40: 7546-52.
- [27] Zhao SJ, Huang JJ, Huo QY, Zhou XZ, Tu WX. A non-noble metal $\text{MoS}_2\text{-Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ photocatalyst with efficient activity for high H_2 evolution under visible light irradiation. *J. Mater. Chem. A* 2016; 4: 193-9.
- [28] Chen XB, Liu L, Yu PY, Mao SS. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* 2011; 331 : 746-50.
- [29] Silva CG, Juarez R, Marino T, Molinari R, Garcia H. Influence of excitation wavelength (UV or Visible Light) on the photocatalytic activity of titania containing gold nanoparticles for the generation of hydrogen or oxygen from Water. *J Am Chem Soc* 2011; 133: 595-602.
- [30] Chen XB, Shen SH, Guo LJ, Mao SS. Semiconductor-based photocatalytic hydrogen generation. *Chem Rev* 2010; 110: 6503-70.
- [31] Bamwenda GR, Tsubota S, Nakamura T, Haruta M. Photoassisted hydrogen production from a water-ethanol solution: a comparison of activities of Au/TiO_2 and Pt/TiO_2 . *J Photochem Photobiol A* 1995; 89: 177-89.

- [32] Bao NZ, Shen LM, Takata T, Domen K. Self-templated synthesis of nanoporous CdS nanostructures for highly efficient photocatalytic hydrogen production under visible light. *Chem Mater* 2007; 20: 110-17.
- [33] Maeda K, Teramura K, Lu DL, Saito N, Inoue Y, Domen K. Noble-metal/Cr₂O₃ Core/Shell nanoparticles as a cocatalyst for photocatalytic overall water splitting. *Angew Chem Int Ed* 2006; 45: 7806-09.
- [34] Xu JB, Zhao TS, Liang ZX, Zhu LD. Facile preparation of AuPt alloy nanoparticles from organometallic complex precursor. *Chem Mater* 2008; 20: 1688-90.
- [35] Liang GF, He LM, Arai M, Zhao FY. The Pt-enriched PtNi alloy surface and its excellent catalytic performance in hydrolytic hydrogenation of cellulose. *Chem Sus Chem* 2014; 7: 1415-21.
- [36] Motl NE, Bondi JF, Schaak RE. Synthesis of colloidal Au–Cu₂S heterodimers via chemically triggered phase segregation of AuCu nanoparticles. *Chem Mater* 2012; 24: 1552-4.
- [37] Kong C, Min SX, Lu GX. Robust Pt–Sn alloy decorated graphene nanohybrid cocatalyst for photocatalytic hydrogen evolution. *Chem Comm* 2014; 50: 9281-3.
- [38] Mentin O, Sun XL, Sun SH. Monodisperse gold–palladium alloy nanoparticles and their composition-controlled catalysis in formic acid dehydrogenation under mild conditions. *Nanoscale* 2013; 5: 910-2.
- [39] Xiao Q, Sarina S, Jaatinen E, Jia JF, Arnold DP, Efficient photocatalytic Suzuki cross-coupling reactions on Au–Pd alloy nanoparticles under visible light irradiation. *Green Chem* 2014; 16:4272-85.
- [40] Su R, Tiruvalam R, He Q, Dimitratos N, Kesavan L, Hammond C. Promotion of phenol photodecomposition over TiO₂ using Au, Pd, and Au-Pd nanoparticles. *ACS Nano* 2012; 6: 6284-97.
- [41] Bonarowska M, Pielaszek J, Juszczak W, Karpinski Z. Characterization of Pd–Au/SiO₂ catalysts by X-ray diffraction, temperature-programmed hydride decomposition, and catalytic Probes. *J Catal* 2000; 195: 304-15.

- [42] Han CC, Wu LE, Ge L, Li YJ, Zhao Z. AuPd bimetallic nanoparticles decorated graphitic carbon nitride for highly efficient reduction of water to H₂ under visible light irradiation. *Carbon* 2015; 1:31-40.
- [43] Xin YJ, Wu LE, Ge L, Han CC, Li YJ, Fang SM. Gold–palladium bimetallic nanoalloy decorated ultrathin 2D TiO₂ nanosheets as efficient photocatalysts with high hydrogen evolution activity. *J Mater Chem A* 2015; 3: 8659-66.
- [44] Savant VV, Gopalakrishnan J, Patel CC. Metal monothiobenzoates. *Inorg Chem* 1970; 9: 748-51
- [45] Su R, Tiruvalam R, Logsdail AJ, He Q, Downing CA, Jensen MT. Designer titania-supported Au–Pd nanoparticles for efficient photocatalytic hydrogen production. *ACS Nano* 2014; 8:3490-7.
- [46] Zhang X, Zhang LZ, Xie TF, Wang DJ. Low-temperature synthesis and high visible-light-induced photocatalytic activity of BiOI/TiO₂ heterostructures. *J Phys Chem C* 2009; 113: 7371-8.
- [47] Laajalehto K, Kartio I, Nowak P. XPS study of clean metal sulfide surfaces. *Appl Surf Sci* 1994; 81:11-5.
- [48] Li Q, Meng H, Zhou P, Zheng YQ, Wang J, Yu JG, Gong JR. Zn_{1-x}Cd_xS solid solutions with controlled bandgap and enhanced visible-light photocatalytic H₂-production activity. *ACS Catal* 2013;3: 882-9.
- [49] Li TQ, Zhou HH, Huang JQ, Yin JL, Chen ZX, Liu D. Facile preparation of Pd–Au bimetallic nanoparticles via in-situ self-assembly in reverse microemulsion and their electrocatalytic properties. *Colloid Surface A* 2014; 463: 55-62.
- [50] Cybula A, Priebe JB, Pohl MM, Sobczak JW, Schneider M, Jurek AZ. The effect of calcination temperature on structure and photocatalytic properties of Au/Pd nanoparticles supported on TiO₂. *Appl Catal B Environ* 2014; 152-153, 202-11.

Figure Captions:

Fig. 1. XRD patterns of AuPd/Cd_{0.5}Zn_{0.5}S composite photocatalysts.

Fig.2. TEM images of (a) Cd_{0.5}Zn_{0.5}S ; (b,c) AuPd/Cd_{0.5}Zn_{0.5}S composite and (d) HRTEM image of AuPd/Cd_{0.5}Zn_{0.5}S composite .

Fig. 3. DRS spectra of the AuPd/Cd_{0.5}Zn_{0.5}S composite samples with different AuPd alloy NP contents.

Fig. 4. XPS spectra of the AuPd/Cd_{0.5}Zn_{0.5}S sample: (a) Zn 2p; (b) Cd 3d; (c) S 2p; (d) Pd 3d; (e) Au 4f ; (f) survey.

Fig. 5. Photocatalytic H₂ evolution over AuPd/Cd_{0.5}Zn_{0.5}S composite samples with different AuPd NPs contents under visible light: (a) 0% AuPd; (b) 0.5wt% Au; (c) 2.0wt AuPd; (d) (d) 0.5 wt% (Au+Pd)/Cd_{0.5}Zn_{0.5}S; (e) 0.1wt% AuPd; (f) 0.5wt% Pd; (g) 1.0wt% AuPd; (h) 0.3wt% AuPd; (i) 0.5wt% AuPd.

Fig. 6. Rate of H₂ evolution over AuPd/Cd_{0.5}Zn_{0.5}S composite samples with different AuPd contents, Pd/Cd_{0.5}Zn_{0.5}S, Au/Cd_{0.5}Zn_{0.5}S and (Au+Pd)/ Cd_{0.5}Zn_{0.5}S under visible light.

Fig. 7. Cycling runs for the photocatalytic H₂ evolution in the presence of the 0.5 wt% AuPd/Cd_{0.5}Zn_{0.5}S composite sample under visible light irradiation.

Fig. 8. (a) Schematic illustration for the charge transfer and separation in AuPd/Cd_{0.5}Zn_{0.5}S system; (b) proposed mechanism for photocatalytic H₂ production under visible light irradiation.

Fig. 9. SPV spectra of AuPd/Cd_{0.5}Zn_{0.5}S photocatalyst with different AuPd NPs content.

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Proposed mechanism for photocatalytic H_2 production under visible light irradiation

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