Journal of Catalysis 266 (2009) 165–168

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt–PdS/CdS photocatalyst

Hongjian Yan [a,1], Jinhui Yang [a,b,1], Guijun Ma [a,b], Guopeng Wu [a], Xu Zong [a,b], Zhibin Lei [a], Jingying Shi [a], Can Li [a,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 3 May 2009
Revised 24 June 2009
Accepted 29 June 2009
Available online 3 August 2009

Keywords:
Photocatalysis
Hydrogen
Cocatalyst
Quantum efficiency
Cadmium sulfide

ABSTRACT

To efficiently convert solar energy into chemical energy by artificial photosynthesis, we need to develop visible-light-responsive photocatalysts with a high quantum efficiency (QE). Here we report that an artificial photocatalyst (Pt–PdS/CdS) can achieve a QE up to 93% in photocatalytic H_2 production in the presence of sacrificial reagents under visible light irradiation, and is very stable under the photocatalytic reaction conditions. The extremely high QE could be achieved by loading as low as 0.30 wt% of Pt and 0.13 wt% of PdS as cocatalysts on CdS.

1. Introduction

The photocatalytic production of hydrogen from water to store solar energy, mimicking thus natural photosynthesis by converting light into chemical energy, has attracted increased attentions recently [1–3]. Most of the developed photocatalysts capable of splitting water can only utilize ultraviolet irradiation constituting only 4% of the incoming solar energy [2–4]. And many researchers have focused on the development of visible-light-responsive photocatalysts in order that the abundant visible light ($\lambda > 420$ nm) which occupies about 43% of the solar energy can be utilized [2,3,5]. A key issue with regard to the conversion of solar energy into chemical energy is the QE of photocatalysts [3]. In the primary course of natural photosynthesis, the overall QE can be as high as 95% [6]. Among the reported visible-responsive chemical photocatalysts up to now [2,3], the highest QE for H_2 production is still 60% over Pt-loaded CdS catalyst [7].

The previous researches on photocatalytic water splitting using chemical photocatalysts have been focused on the development of semiconductor-based photocatalytic materials, while the exploration of cocatalysts is less concerned with this issue [3]. Although certain photocatalysts have been found to exhibit high photocatalytic activity even without cocatalysts, in most cases, cocatalysts enable or increase the photocatalytic activity of a semiconductor [2]. The cocatalysts could function as active sites for reduction or oxidation and/or suppress the back reaction of water formation from evolved H_2 and O_2, etc. [2]. Noble metals (e.g., Pt, Pd, Ru, and Rh) [2], transition metal oxides (e.g., NiO [4] and $Rh_{2-y}Cr_yO_3$ [1]) and transition metal sulfides (e.g., MoS_2 [8]) have been found to be effective for facilitating H_2 evolution. Some transition metal oxides (e.g., RuO_2 and IrO_2) are found to be good oxidation cocatalysts for O_2 evolution, although RuO_2 is also found to be a reduction cocatalyst [9]. Up to date, only a few researches have shown that suitable dual cocatalysts could increase the photocatalytic activity of a semiconductor catalyst [10].

Here we report that CdS co-loaded with Pt and PdS (denoted as Pt–PdS/CdS) can achieve a QE up to 93% at 420 nm for photocatalytic H_2 production using sulfide and sulfite as sacrificial reagents. Furthermore, the Pt–PdS/CdS catalyst does not show deactivation for H_2 evolution for longer than 100 h.

2. Experimental

2.1. Preparation of the catalysts

All the reagents were of analytical grade, and were used without further purification.

The CdS nanoparticles were prepared as follows: an aqueous solution of Na_2S (800 mL, 0.14 M) was added slowly to $Cd(OAc)_2$

---

* Corresponding author. Fax: +86 411 84694447.
E-mail address: canli@dicp.ac.cn (C. Li).
URL: http://www.canli.dicp.ac.cn (C. Li).
[1] Both authors contributed equally to this work.

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.06.024

solution (1000 mL, 0.14 M) under vigorous stirring. The yellow mixture was stirred for 24 h and kept for an additional 24 h. The resulting yellow slurry was filtered. The wet solid was suspended in pure water (120 mL) and transferred to a Teflon-lined stainless steel autoclave (150 mL) and heated at 473 K for 72 h (hydrothermal treatment). The yellow solid was filtered, washed with water and ethanol subsequently, filtered again, and kept under vacuum at 368 K for 24 h.

The loading or co-loading of Pt and Pd on CdS producing Pt/CdS, Pd/CdS, and Pt–Pd/CdS was done by photodeposition. Thus, for example, H_2PtCl_6 aqueous solution (0.0019 M) was added to a suspension of CdS (1 g, as prepared above) dispersed in acetic acid (AcOH, 80 mL, 0.25 M) and containing $Cd(Ac)_2{\cdot}2H_2O$ (0.5 g). The mixture was deaerated under vacuum and then irradiated with 300 W Xe lamp for 30 min. The resulting suspension was then filtered, washed with water, and dried at 363 K under vacuum.

The loading of PdS on CdS producing PdS/CdS was realized by in-situ deposition. Thus, for example, a $PdCl_2$ aqueous solution (0.0011 M) was added dropwise to a suspension of CdS powder (0.3 g, as prepared above) dispersed in Na_2S aqueous solution (0.5 M) just before the photocatalytic reaction.

The co-loading of Pt and PdS on CdS producing Pt–PdS/CdS was realized similar to the loading of PdS except for the additional addition of a H_2PtCl_6 aqueous solution (0.0019 M).

2.2. Characterization

The phase of the as-prepared CdS was examined by X-ray diffraction (Rigaku; MiniFlex diffractometer with a Cu Kα irradiation source). Diffraction patterns were collected from 20° to 80° at a speed of $5^\circ\ \mathrm{min}^{-1}$. The Ultraviolet-visible diffuse reflectance spectra (UV–vis DRS) were obtained using a JASCO V-550 spectrophotometer. The size and morphology were examined with Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM images were obtained on a Quanta 200F microscope (FEI Company) with the accelerating voltage of 0.5–30 kV. TEM images were obtained on Tecnai G^2 Spirit (FEI Company) microscopy with the accelerating voltage of 120 kV.

2.3. Photocatalytic reaction test

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Photocatalyst, 0.3 g, was dispersed in 200 mL of aqueous solution containing 0.5 M Na_2S and 0.5 M Na_2SO_3 as the sacrificial reagents. The suspension was then thoroughly degassed and irradiated by a 300 W Xe lamp (ILC technology; CERAMAX LX-300) which is equipped with an optical filter (HOYA, $\lambda > 420$ nm) to cut off the light in the ultraviolet region. The temperature of the reaction solution was maintained at 12–18 °C by a flow of cooling water. The amount of hydrogen evolved was determined with on-line gas chromatography (Shimadazu; GC-8A, MS-5 A column, TCD, Ar Carrier).

Table 1
Photocatalytic H_2 evolution over CdS loaded with various cocatalysts.

Catalyst	H_2 evolution rate ($\mathrm{mmol\ h^{-1}}$)[a]	QE (%)
CdS	0.023	0.2
Pd/CdS	3.82	40
Pt/CdS	4.80	51
Pt–Pd/CdS	4.95	53
PdS/CdS	5.99	64
Pt–PdS/CdS	8.77	93

[a] Experiments were done using 0.3 g of photocatalysts powder suspended in 200 mL of 0.5 M Na_2S-0.5 M Na_2SO_3 solution in a pyrex glass cell under visible light irradiation ($\lambda > 420$ nm). Light source: 300 W Xe lamp. Loading amount: 1 wt%.

The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition with irradiation light at 420 nm by using combined band-pass (Kenko) and cut-off filters (HOYA) and 300 W Xe lamp, and the QE was calculated according to Eq. (1):

$$\mathrm{QE}\ [\%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 = \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \qquad (1)$$

The number of incident photons was 3.54×10^{17} photons/s which was measured by using a calibrated Si photodiode (HAMAMATSU S2281). The number of incident photons was also calibrated with ferrioxalate solution in the same device [11].

3. Results and discussion

Well-crystallized cadmium sulfide (CdS) nanoparticles possess hexagonal structures and diameters of approximately 40–60 nm (Supplementary material, Figs. 1 and 2) and their UV–vis diffuse reflectance spectrum shows an absorption edge at about 540 nm (2.3 eV) (Supplementary material, Fig. 3).

In Table 1, the photocatalytic activities (or QE) for H_2 evolution over CdS, Pt/CdS, Pd/CdS, Pt–Pd/CdS, and Pt–PdS/CdS catalysts are given. CdS without the cocatalysts loaded exhibits very low photocatalytic activity for H_2 evolution (*ca.* $0.023\ \mathrm{mmol\ h^{-1}}$), and the activity is enhanced markedly by loading noble metals such as Pd and Pt as cocatalysts, while the activity is hardly increased further when Pt and Pd are co-loaded. When PdS is employed as the cocatalyst, the photocatalytic activity is even higher than that of Pt/CdS, achieving 280 times higher activity than that of CdS alone. Most interestingly, the activity is enhanced further to 380 times when Pt and PdS are co-loaded on CdS, and the H_2 evolution rate is estimated to be as high as $8.77\ \mathrm{mmol\ h^{-1}}$, corresponding to a QE of 93% at 420 nm. In our previous work, the co-loading of Pt and PdS on CdS could result in an enhancement of activity in the direct splitting of H_2S to H_2 and S in organic media, although the QE is only about 30% [12].

Fig. 1 shows the reaction time courses for H_2 evolution over Pt/CdS, PdS/CdS, and Pt–PdS/CdS photocatalysts. PdS/CdS and Pt–PdS/CdS exhibit very stable activity during the 25-h irradiation. However, the rate of H_2 production over Pt/CdS gradually decreases

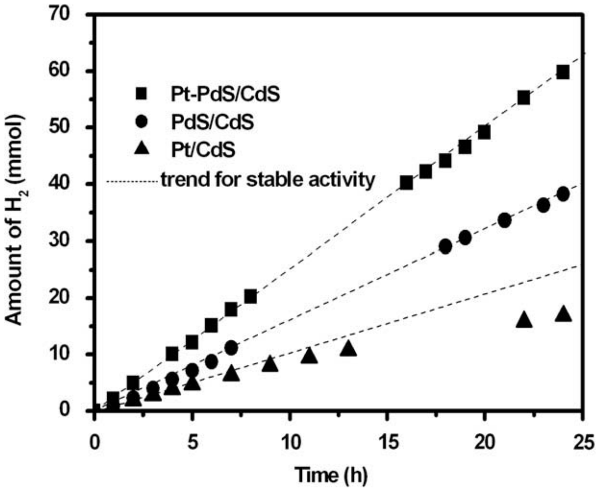

Fig. 1. The time courses of H_2 evolution under visible irradiation over Pt/CdS (▲), PdS/CdS (●), and Pt–PdS/CdS (■). Catalyst: 0.012 g; 0.5 M Na_2S–0.5 M Na_2SO_3 aqueous solution (200 mL); Light source: Xe lamp (300 W) with an optical filter ($\lambda > 420$ nm).

and an evident drop in the activity is found after an irradiation for 10 h. This could be largely attributed to the photocorrosion of CdS [7]. The lifetime experiments of the photocatalysts show that the CdS and Pt/CdS are evidently deactivated, while the PdS/CdS and Pt–PdS/CdS exhibit stable activity even after a photocatalytic reaction for longer than 100 h.

Fig. 2 shows the dependence of the photocatalytic activity on the loading amount of Pt and PdS. For Pt/CdS, the rate of H_2 evolution is increased with the increase of Pt-loading from 0 to 0.65 wt%. When the loading amount of Pt is increased to 0.65 wt%, the activity reaches a maximum, 4.80 mmol $^{-1}$ with a QE of 51%, at 420 nm. This activity is close to that recently reported for Pt/CdS by Domen et al. [7]. The rate of H_2 evolution over PdS/CdS shows a similar trend, but only 0.13 wt% PdS achieved a maximum activity as high as 5.99 mmol h^{-1}, corresponding to a QE of 64% at 420 nm. Surprisingly, we found that the activity can be greatly increased further when Pt is co-loaded with PdS on CdS. The maximum activity of 8.77 mmol h^{-1} with a QE of 93% can be achieved by co-loading only 0.30 wt% Pt and 0.13 wt% PdS on CdS.

The chemical states of Pd and Pt on catalysts after photocatalytic reaction were examined by X-ray photoemission spectroscopy (XPS). The results show that the binding energy of Pt (4f7/2) is consistent with Pt^0 (Supplementary material, Fig. 4) [13], and that the dominant valence for the palladium of PdS on CdS collected after the photocatalytic reaction is Pd^{II}, while a small portion of metallic Pd also exists, indicating a partial photoreduction of PdS during the photocatalytic reaction. The amount of Pd^0 is only about 1/20 of that of Pd^{II} in PdS (Fig. 3) [14].

To testify whether such a low amount of metallic Pd is due to the reaction of Na_2S with Pd during the post-treatment, the PdS/CdS material was collected after photocatalytic reaction. It was redispersed in Na_2SO_3 aqueous solution (without Na_2S) and collected again after an irradiation for 3 h. The XPS spectra shown in Fig. 3 reveal the coexistence of metallic Pd and PdS with the ratio of Pd^0 to Pd^{II} in PdS up to 2.8. This indicates the formation of metallic Pd during the photocatalytic reaction. On the other hand, the reduction potential of PdS/Pd ($E_{PdS/Pd}$) (−0.84 V vs. NHE), comparable to that of H_2O/H_2(−0.80 V vs. NHE), makes the photoreduction of PdS possible. Thus, a QE as high as 64% in photocatalytic hydrogen production achieved on PdS/CdS might be due to the synergetic effect of PdS and metallic Pd.

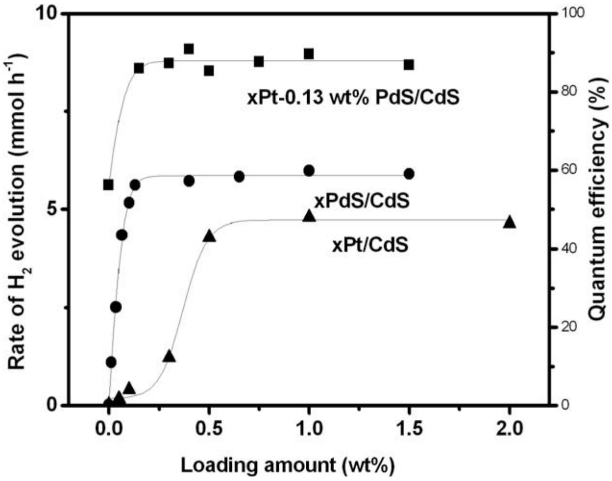

Fig. 2. The rate of H_2 evolution as a function of the loading amount of Pt and PdS. x denotes the loading amount. The lower curve shows the dependence of activity of Pt/CdS on the loading amount of Pt; the middle curve shows the dependence of activity of PdS/CdS on the loading amount of PdS. The uppermost curve shows the dependence of the activity of Pt-0.13 wt% PdS/CdS on the loading amount of Pt. The highest QE (93%) was obtained through co-loading 0.13 wt% PdS and 0.3 wt% Pt on CdS. Catalyst: 0.3 g; 0.5 M Na_2S–0.5 M Na_2SO_3 aqueous solution (200 mL); Light source: Xe lamp (300 W) with an optical filter (λ > 420 nm).

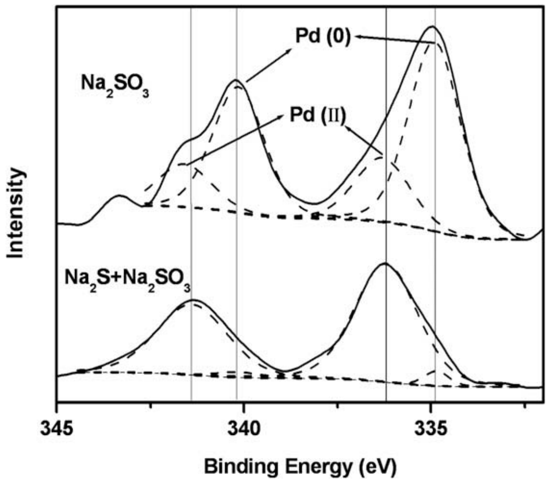

Fig. 3. X-ray photoelectron spectra (XPS) of Pd 3d in the Pt–PdS/CdS catalyst collected after an irradiation with visible light (λ > 420 nm) for 3 h in 0.5 M Na_2SO_3 (upper) and 0.5 M Na_2S–0.5 M Na_2SO_3 (lower) aqueous solutions. The solid curves are the smoothing original data. The dashed lines are composite fits of Pd^{II} and Pd^0. The lines were fitted by 80% Gaussian and 20% Lorentz functions after Shirley background subtraction. Palladium $3d_{5/2}/3d_{3/2}$ intensity ratio was set to 3:2 and the Binding Energy difference was 5.25 eV. The data were calibrated by C1s at 284.6 eV. The atomic ratio of Pd^{II} to Pd^0 is determined according to the peak area [15].

The direction of charge transfer between the components could be predicted according to their energy band structures [16]. It has been reported that PdS is an n-type semiconductor with a band gap of 1.60 eV [17]. The conduction band edge of PdS is estimated to be −0.5 V vs. SCE (−0.26 V vs. NHE) (Supplementary material, Fig. 5) by Mott-Schottky analysis [18], and the valence band potential of PdS deduced from the conduction band and the band gap (1.6 eV) is approximately +1.34 V vs. NHE, which is less positive than that of CdS (+1.5 V) [2]. This implies that the hole transfer from CdS to PdS is a favorable process, and that the PdS could act as an oxidation cocatalyst here. The conduction band edge of PdS is less negative than the H_2O/H_2 redox potential (−0.80 V vs. NHE) under the photocatalytic condition (pH = 13.6), so PdS by itself displays no photocatalytic activity for H_2 production.

Therefore, the simultaneous existence of PdS acting as an oxidation cocatalyst and Pt (or Pd) acting as a reduction cocatalyst is supposed to be beneficial for the efficient separation and transfer of the photoexcited electrons and holes, thus contributing to the extremely high QE. The PdS acting as the oxidation cocatalyst can also protect CdS from photocorrosion, and can make the PdS/CdS and Pt–PdS/CdS very stable under the photocatalytic reaction conditions. Further work is underway to establish the roles of the dual cocatalysts in photocatalytic H_2 production.

4. Conclusions

In summary, an extremely high QE for H_2 production has been achieved over Pt–PdS/CdS photocatalysts. The Pt–PdS/CdS catalyst demonstrates the possibility of realizing visible-light-responsive photocatalytic hydrogen production with a QE approaching the level of natural photosynthesis. The strategy to achieve high QE by co-loading suitable dual cocatalysts, especially those functioning as oxidation and reduction cocatalysts, respectively, will be of considerable importance in the design and preparation of highly active photocatalysts for solar energy conversion.

Acknowledgments

This work was finacially supported by National Program on Key Basic Research Project (Grant No.: 2009CB220010) and Solar Energy Action Project of Chinese Academy of Sciences. The authors acknowledge Prof. Alain Krief for his kind suggestion for the manuscript revision.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.06.024.

References

[1] K. Maeda, K. Teramura, D.L. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, Nature 440 (2006) 295.
[2] F.E. Osterloh, Chem. Mater. 20 (2008) 35.
[3] A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253.
[4] H. Kato, K. Asakura, A. Kudo, J. Am. Chem. Soc. 125 (2003) 3082.
[5] I. Tsuji, H. Kato, A. Kudo, Angew. Chem. Int. Ed. 44 (2005) 3565.
[6] V. Sundström, T. Pullerits, R. van Grondelle, J. Phys. Chem. B 103 (1999) 2327.
[7] N.Z. Bao, L.M. Shen, T. Takata, K. Domen, Chem. Mater. 20 (2008) 110.
[8] X. Zong, H.J. Yan, G.P. Wu, G.J. Ma, F.Y. Wen, L. Wang, C. Li, J. Am. Chem. Soc. 130 (2008) 7176.
[9] T. Sakata, K. Hashimoto, T. Kawai, J. Phys. Chem. 88 (1984) 5214.
[10] K. Maeda, K. Teramura, N. Saito, Y. Inoue, K. Domen, J. Catal. 243 (2006) 303.
[11] J. Lee, H.H. Seliger, J. Chem. Phys. 40 (1964) 519.
[12] G. Ma, H. Yan, J. Shi, X. Zong, Z. Lei, C. Li, J. Catal. 260 (2008) 134.
[13] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin–Elmer Corp., Physical Electronics Division, USA, 1992.
[14] J.A. Rodriguez, T. Jirsak, S. Chaturvedi, J. Chem. Phys. 110 (1999) 3138.
[15] Y. Boudeville, F. Figueras, M. Forissier, J. Portefaix, J.C. Vedrine, J. Catal. 58 (1979) 52.
[16] T. Kida, G.Q. Guan, Y. Minami, T.L. Ma, A. Yoshida, J. Mater. Chem. 13 (2003) 1186.
[17] I.J. Ferrer, P. Díaz-Chao, A. Pascual, C. Sánchez, Thin Solid Films 515 (2007) 5783.
[18] K. Sayama, A. Nomura, T. Arai, T. Sugita, R. Abe, M. Yanagida, T. Oi, Y. Iwasaki, Y. Abe, H. Sugihara, J. Phys. Chem. B 110 (2006) 9.