

Xiaoping CHEN, Wenfeng SHANGGUAN

Hydrogen production from water splitting on CdS-based photocatalysts using solar light

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Abstract Hydrogen energy has been regarded as the most promising energy resource in the near future due to that it is a clean and sustainable energy. And the heterogeneous photocatalytic hydrogen production is increasingly becoming a research hotspot around the world today. As visible light response photocatalysts for hydrogen production, cadmium sulfide (CdS) is the most representative material, the research of which is of continuing popularity. In the past several years, there has been significant progress in water splitting on CdS-based photocatalysts using solar light, especially in the development of co-catalysts. In this paper, recent researches into photocatalytic water splitting on CdS-based photocatalysts are reviewed, including controllable synthesis of CdS, modifications with different kinds of cocatalysts, solid solution, intercalated with layered nanocomposites and metal oxides, and hybrids with graphenes etc. Finally, the problems and future challenges in photocatalytic water splitting on CdS-based photocatalysts are described.

Keywords hydrogen, photocatalysis, solar conversion, cadmium sulfide (CdS) complex

1 Introduction

As fossil fuels are likely to be exhausted in the near future and bring lots of serious environmental problems, hydrogen, a new renewable and no-polluting energy, has been considered as a promising candidate to solve these problems. There are different ways to get hydrogen from water such as electrolysis of water, but most of them are costly. In various interesting reactions, the hydrogen

production from photocatalytic water splitting by sunlight is potentially one of the most promising ways for the photochemical conversion and storage of solar energy. Since the evolution of hydrogen and oxygen on TiO₂ and Pt counter electrodes under the irradiation of ultraviolet (UV) light was reported by Fujishima and Honda in 1972 [1], photocatalysis has been receiving much attention and studies have been extensively conducted on converting solar energy into clean hydrogen energy. The mechanism of photocatalytic of water is illustrated in Fig. 1, in which TiO₂ was taken as an example [2]. The band gap (between valance band and conductance band) of TiO₂ is approximately 3.0 eV. Electronic transition from valance band to conductance band can be activated by light radiation whose energy should be greater than or equal to its band gap. Consequently, the electron and hole pairs are formed in conductance band and valance band, which can decompose water into hydrogen and oxygen respectively. Up to the present, various kinds of efficient hydrogen-evolution photocatalysts have been reported which can mainly be divided into the titanium dioxide system [3–7] which also contains hybrids of TiO₂ [8,9]; metal sulfides, nitrides and phosphides [10–13]; the tantalate and niobate system [14–18]; and composite catalysts [19–23]. However, most of these photocatalysts are only active under UV light, which accounts for only approximately 3%–5% of the solar spectrum on the surface of the earth.

Cadmium sulfide (CdS) has a band-gap energy (E_g) of 2.4 eV that suits very well with the solar spectrum as shown in Fig. 2, which has received much attention and has been studied widely. However, CdS is not stable in aqueous solutions under irradiation due to photocorrosion. Furthermore, the photocatalytic activity of individual CdS is not so efficient. In order to solve these problems, many researchers mainly focus their attention on material preparation, where different morphology and crystal CdS are synthesized; material modifications; and the system of photocatalytic water splitting to improve the photoactivity.

In this paper, the current research focuses on the improvement of CdS photocatalytic activity are reviewed

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Xiaoping CHEN, Wenfeng SHANGGUAN (✉)
Research Center for Combustion and Environment Technology,
Shanghai Jiao Tong University, Shanghai 200240, China
E-mail: shangguan@sjtu.edu.cn

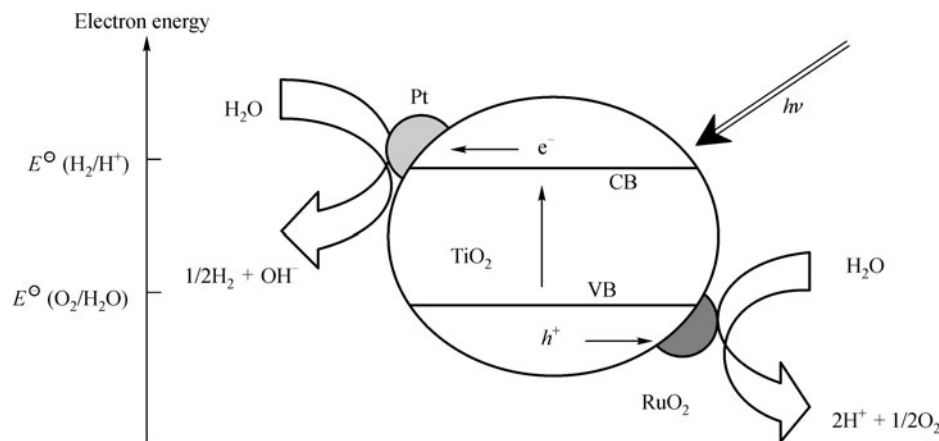


Fig. 1 Mechanism of the photocatalytic of water into H_2 and O_2 on TiO_2 [2]

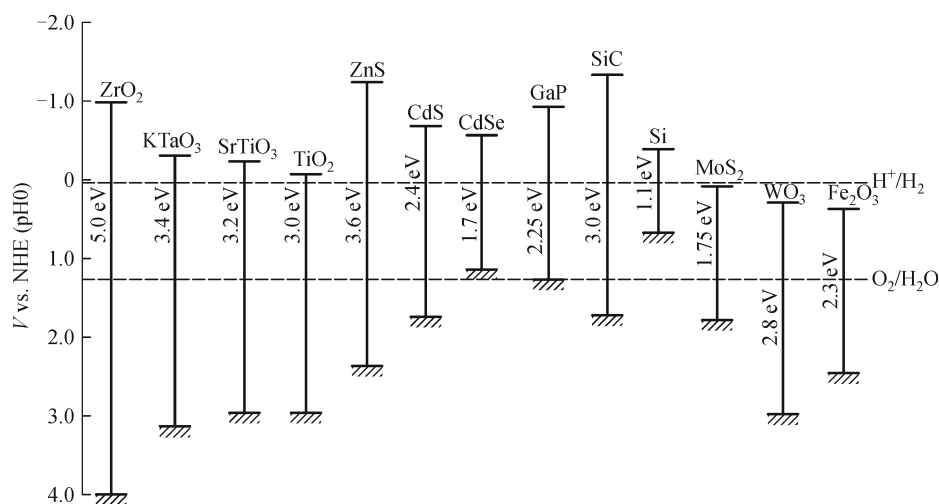


Fig. 2 Relationship between band structure of semiconductor and redox potentials of water splitting [24]

and discussed. In addition, future trends of research on photocatalytic water splitting with CdS are presented.

2 Controllable synthesis of CdS for photocatalytic hydrogen evolution

The photocatalytic properties of CdS semiconductor materials depend not only on the particle size but also the morphology [25–27]. So different synthesis methods are attempted to prepare CdS with different nanostructured and high BET surface area for improving its photoactivity [28–32]. Liu et al. [28] have prepared CdS hollow nanoparticle chains through a facile and efficient ultrasonic-template method. Other shapes of CdS nanostructures, such as nanorods, hollow nanorods, multipods, quasi-nanospheres, hollow nanospheres, nanoshuttles, nanowires, nanotubes, nanosheets have also been reported [29–32]. Li et al. [31] have obtained solid nanospheres (s-CdS), hollow nanospheres (h-CdS) and nanorods (r-CdS)

by controlling only the hydrothermal temperatures. They have also revealed the performance of different hydrogen evolutions as presented in Fig. 3. Bao et al. [32] synthesized porous nanosheets and hollow nanorods CdS by a two-step aqueous route. The quantum yield could come to 60.34% at 420 nm after loaded with Pt.

Quantum dots are also used to improve the photocatalytic activity of catalysts because of its special properties. Yu et al. [33] prepared CdS quantum dots-sensitized $Zn_{1-x}Cd_xS$ solid solutions by a simple cation exchange. It showed high visible-light photocatalytic H_2 -production activity even without a Pt co-catalyst.

3 Modifications of CdS

3.1 Loaded with cocatalysts

Besides preparing CdS with different morphology and particle size, co-catalysts also play an important role in

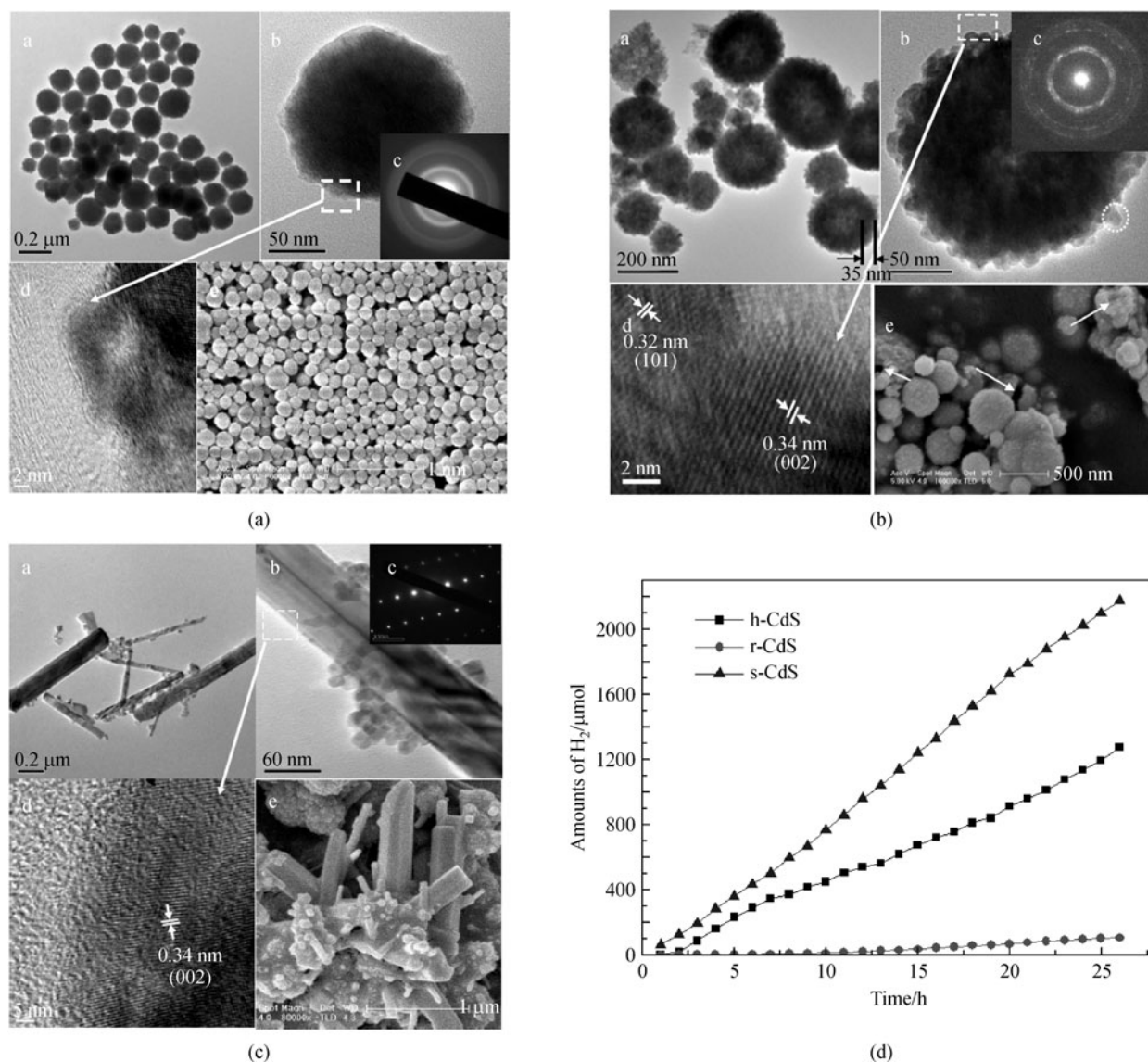


Fig. 3 Electron microscopic photos [30]

(a) Solid nanospheres (s-CdS); (b) hollow nanospheres (h-CdS); (c) nanorods (r-CdS); (d) hydrogen evolution activity

stimulating charge transfer and reducing the recombination of photo-induced charges, thereby enhancing the photocatalytic activity of CdS. The efficient photocatalytic co-catalysts usually contain noble metals (Pt, Au, Rh, RuO₂, etc.) [34–39]. Luo et al. [39] have prepared CdS loaded with dual co-catalysts including PdS and Pt as the oxidation and reduction co-catalysts, respectively. As demonstrated in Fig. 4, electrons and holes can be transferred at the same time. The quantum efficiency of photocatalytic hydrogen production can reach 93% in the presence of sacrificial reagents under visible light.

Although good photocatalytic performance of CdS can be achieved in the presence of noble metals co-catalysts, it is necessary to explore non-noble metals to reduce the cost of renewable H₂ production. The traditional efficient non-noble metals co-catalysts are nickels (Ni, NiO, NiS, NiO_x)

[38–40]. However, several researches have focused on the modification of CdS with metal sulfides (MoS₂, WS₂) recently, which supplies a new way to improve the performance of CdS [41,42]. MoS₂ is an excellent H₂ evolution co-catalyst. Furthermore, the junctions formed between MoS₂ and CdS also play an important role in enhancing the photocatalytic activity of CdS. Thus, the 0.2 wt% MoS₂/CdS catalyst demonstrates even higher activity than other noble metal co-catalysts as tabulated in Table 1 [42]. W₂S plays the same role as MoS₂ in enhancing the photocatalytic activity of CdS [41].

3.2 Intercalated with layered nanocomposites and metal oxides

In order to improve the photocatalytic properties, CdS

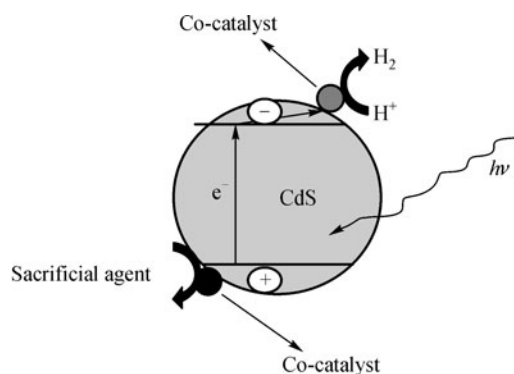


Fig. 4 Mechanism of photocatalytic H₂ evolution on CdS loaded with co-catalysts

Table 1 Rate of H₂ evolution on CdS loaded with different co-catalysts under visible light ($\lambda > 420$ nm)

Sample	Evolved H ₂ /($\mu\text{mol}\cdot\text{h}^{-1}$)	Reaction conditions
CdS	15	0.1 g catalyst
1 wt% Pt/CdS	355	10% (vol) lactic solution (200 mL); light source, xenon
1 wt% Ru/CdS	293	Lamp (300 W) with a cutoff filter
1 wt% Rh/CdS	207	
1 wt% Au /CdS	45.5	
0.1 wt% WS ₂ /CdS	420	
0.2 wt% MoS CdS	533	

nanoparticles are often incorporated in the interlayer of some particulate metal oxides. As shown in Fig. 5, the incorporation of CdS nanoparticles into the interlayer of layered metal oxides suppresses particle growth while nanoheterojunctions are formed easily between the host layer and the CdS. Thus, photogenerated electrons are quickly transferred through the nanostructure while the recombination between the photo-induced electron and the hole is effectively suppressed. Consequently, the photocatalytic evolution of hydrogen is enhanced [38].

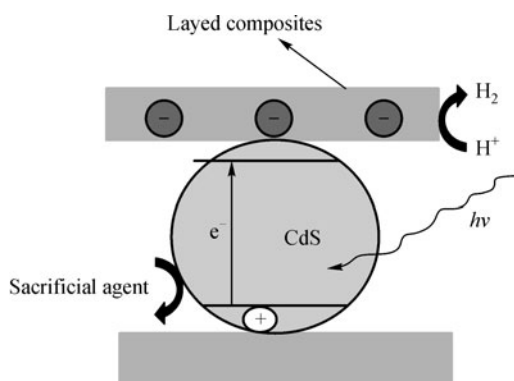


Fig. 5 Mechanism of photocatalytic H₂ evolution on CdS intercalated with layered nanocomposites

As listed in Table 2, the photocatalytic hydrogen evolution of CdS intercalated with layered nanocomposites is superior to simple CdS and the physical mixture of CdS and metal oxides. Further, the activity of CdS intercalated with layered nanocomposites is dependent on hostlayer. The substitution of Nb for partial Ti can bring the quick transfer of the electrons photogenerated in CdS through the host layer into the surface of photocatalysts, Thus, the hydrogen evolution increases [38].

Recently, the Z-scheme has been investigated to split water into hydrogen and oxygen [43,44]. Tada et al. [45] have designed a CdS-Au-TiO₂ three-component nanojunction system imitating natural photosynthesis. This three-component system exhibit a high photocatalytic activity, far exceeding those of the single- and two-component systems, as a result of vectorial electron transfer driven by the two-step excitation of TiO₂ and CdS.

Other CdS intercalated with metal oxides or sulfides and the heterojunction between them have also been extensively studied [46–51]. Barpuzary et al. [51] have prepared high surface area CdS using Al₂O₃ and ZnO as templates by a hydrothermal route. The apparent quantum yields of hetero-system-based CdS@Al₂O₃ and CdS@ZnO can account to 11% and 15% respectively. One-dimensional heterostructures of CdS nanowires decorated with hematite nanoparticles and magnetite microsphere have been synthesized via a two-step solvothermal deposition method [52]. The enhanced photocatalytic activity under visible light happens on account of the help of heterostructures, which can facilitate charge separation. Li et al. [53] have fabricated CdS/TiO₂NTs in which CdS is incorporated into the TiO₂ nanotubes homogeneously. Because of the quantum size effect and the potential gradient at the interface between CdS nanoparticles and TiO₂ nanotubes, the CdS/TiO₂NTs showed higher activity for hydrogen production under visible light.

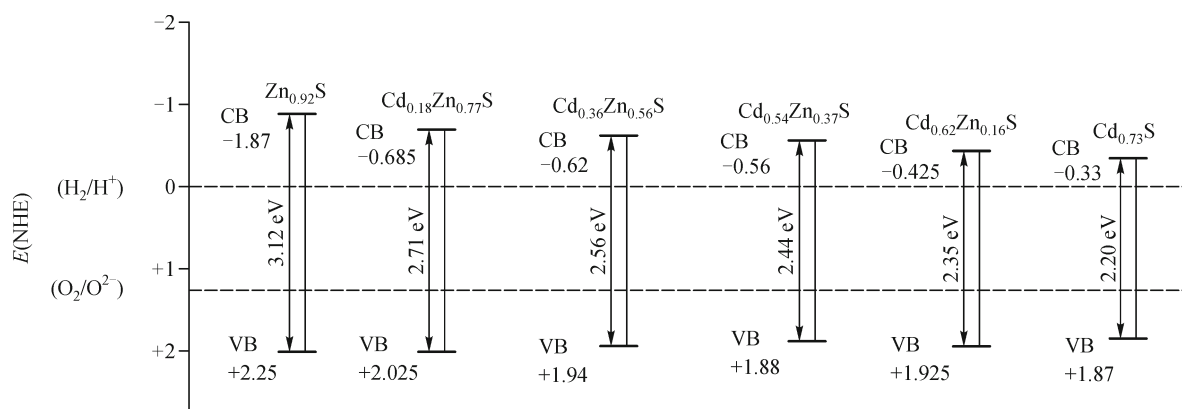
3.3 Solid solution

The solid solution is often used as an efficient way to improve the activity and stability of CdS [54–57]. With the help of insert metals, the electron-hole recombination and photocorrosion can be prevented efficiently. Therefore, the photocatalytic activity and stability of catalysts can be enhanced apparently [55]. For instance, Ikeue et al. [56] have synthesized the composite sulfide system (Mn_{1-x}Cd_xS) by a hydrothermal method and found that the high photocatalytic activity of the Mn_{1-x}Cd_xS system is caused by low-crystalline. Moreover, Mn_{1-x}Cd_xS system showed better tolerance to photocorrosion compared to single CdS. On the other hand, the band structure of Mn_{1-x}Cd_xS system could also be controlled through controlling components and their contents of solid solution. As is known, the band gap of CdS and ZnS are 2.20 and 3.12 eV respectively. And the band gap position of the solid solutions can be adjusted by changing the ratio

Table 2 Resultant properties of CdS and CdS-incorporated composites [41]

Sample	Bandgap/eV	CdS content/wt%	Specific surface area/(m ² ·g ⁻¹)	Evolved H ₂ /(mmol·m ⁻² ·h ⁻¹) ^a
CdS ^b	2.4	—	20.5	3.24
CdS/KTiNbO ₅	2.6	6.5	10.3	3.68
CdS/K ₂ Ti ₄ O ₉	2.6	10.2	12.4	3.80
CdS/K ₂ Ti _{3,9} Nb _{0,1} O ₉	2.5	19.5	19.3	4.70
CdS/ K ₂ Ti _{3,9} Nb _{0,1} O ₉ ^c	—	—	—	3.20

Notes: ^a—Rate of H₂ evolution under xenon lamp (300 W) in the aqueous solution of Na₂S (0.1 M, 20 ml); ^b—a neat CdS powder; ^c—physical mixture of 20 wt% CdS + 80 wt% K₂Ti_{3,9}Nb_{0,1}O₉

**Fig. 6** Conduction and valence band potentials of Zn_xCd_{1-x}S [50]

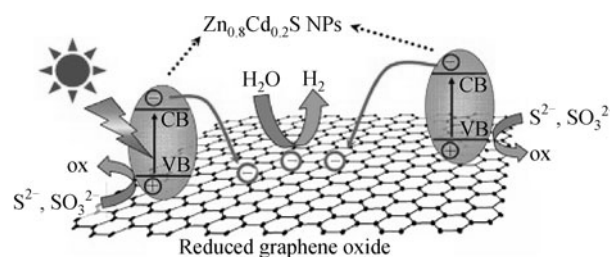
of the composition of CdS to that of ZnS as displayed in Fig. 6 [54], which is important for high efficient and stable photocatalysts design and preparation.

3.4 Hybrids with graphenes

Because of the special conductivity and conjugated system derived from the unique sp² hybrid carbon skeleton structure, graphene has been regarded as an ideal conductive support for nanoparticles to form hybrid materials with CdS for the purpose of photocatalytic activity improvement [58–62]. As exhibited in Fig. 7, CdS or its solid solutions can be excited by solar to generate electrons and holes. Besides the function of heterostructures and high surface area of catalyst hybrids, the photogenerated electrons are transferred to graphene while holes are left in CdS since the conduction band of CdS is more negative [59]. Thus, the recombination of electron-hole pairs is suppressed and the lifetime of charge carriers is prolonged. Consequently, the photoactivity can be improved efficiently and the apparent quantum efficiency can be up to 23.4% at 420 nm [58].

4 Conclusions

In this paper, current researches of hydrogen production with CdS-based photocatalysts are reviewed and dis-

**Fig. 7** Mechanism of photocatalytic hydrogen production on reduced graphene oxide-Zn_xCd_{1-x}S [54]

ussed. Great progress has been made in the research of high efficient photocatalytic hydrogen production with CdS. Through loading cocatalysts, intercalating with layered nanocomposites, hybrids with graphenes or solid solution can favor electron transfer and suppress the recombination of electron-hole pairs. Thus the photocatalytic activity and stability can be improved apparently. These may provide reference for the preparation of more efficient CdS-based photocatalysts for the purpose of hydrogen production. However, few studies on suppressing photocorrosion have been conducted to improve the stability of CdS. Consequently, new and advanced ways have to be further investigated on CdS to enhance its photocatalytic water splitting performance.

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