Enhanced visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ by conduction band co-catalysts (MoO_2 , MoS_2 and MoSe_2)

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ABSTRACT

Several conduction band co-catalysts (CBCOs), MoO_2 , MoS_2 and MoSe_2 , were prepared to improve the visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ from water splitting, in which the PdS is a valence band co-catalyst (VBCO) used to facilitate the photo-generated hole transfer and the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ is an up-conversion luminescence agent from visible light to ultraviolet light used to provide the ultraviolet light satisfying the energy demands of wide band-gap ZnS photocatalyst. XRD, SEM, TEM and EDX analyses were employed to confirm the morphology, microstructure and composition of the prepared photocatalysts. UV-vis absorption and PL spectra were also determined to explore luminescence effect of the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$. The visible-light photocatalytic hydrogen evolution activity of the prepared photocatalysts was evaluated by using Na_2S and Na_2SO_3 as sacrificial reagents in aqueous solution under visible light irradiation. The influential factors such as contents of CBCOs (MoO_2 , MoS_2 and MoSe_2) and visible-light irradiation time on visible-light photocatalytic hydrogen evolution of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($\text{X} = \text{O}, \text{S}$ and Se) were investigated in detail. Particularly, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$ with 0.30 wt% MoSe_2 shows the highest

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photocatalytic hydrogen evolution activity.

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Keywords: Conduction band co-catalyst; Valence band co-catalyst; Visible-light photocatalytic hydrogen evolution; Up-conversion luminescence agent

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Introduction

In order to effectively solve the severe global energy crisis and serious environmental issues resulted from excessive consumption of fossil fuels, many researchers have been exploring the renewable, low cost and clean forms of energy, which will be used as an alternative source to fossil fuels. The solar energy will likely play a key role in the development of new energy sources in some degree. Hydrogen has aroused extensive interest as an energy principal part that offers high energy capacity and low environmental effect. Photocatalytic hydrogen evolution from water splitting under solar radiation represents a promising strategy in the hydrogen evolution [1-6]. Since Honda and Fujishima reported the photocatalytic behavior of TiO_2 firstly in 1972 [7], in recent decades, a series of photocatalysts have been developed for solar water splitting, such as Ta_2O_5 , ZnO , CdS , etc. [8-10]. Among the developed photocatalysts, metal sulfide photocatalysts, especially, ZnS (band gap 3.6 eV), have been

the focus of scientific research owing to their optical properties and unique catalytic functions. However, ZnS is responsive only in ultraviolet light region, which largely limits its application as a photocatalyst. To overcome this disadvantage, many strategies have been used, such as nanomaterials morphology modification and semiconductor coupling. These methods are proved to be effective, but they reduce the original catalytic activity of ZnS. The best way is meeting the energy demands of ZnS with wide band-gap to maintain the catalytic activity [11-17]. Recently, our study suggested that the combination of up-conversion luminescence agent can improve the photocatalytic hydrogen evolution efficiency of some wide band-gap ($E_{bg} \geq 3.00$ eV or $\lambda_{max} \leq 380$ nm) photocatalysts [18-21]. Up-conversion luminescence is an interesting way which can convert two or more low energy photons to a higher energy photon for satisfying the requirements of wide band-gap semiconductor materials. As a visible-to-ultraviolet up-conversion luminescence agent, $Er^{3+}:Y_3Al_5O_{12}$, has attracted significant attention due to the excellent characteristic of chemical and optical properties, which can effectively activate the ZnS to carry out visible-light photocatalytic reaction [22-28].

So far, most inorganic semiconductor materials can not satisfy commendably the requirements for an effectively photocatalytic water splitting [29-32]. A key reason is that the fast recombination of photo-generated electrons and holes decrease the efficiency of most photocatalysts. In order to promote the rapid transfer of photo-generated electrons and holes from photocatalyst, loading co-catalysts is a valid strategy. At present, many kinds of co-catalysts have been studied, including MoO_3 , MoS_2 , $MoSe_2$, RuO_2 and PdS , whereas the roles of co-catalysts in the reaction are different. In general, MoO_3 , MoS_2 and $MoSe_2$ can be used as effective conduction band co-catalysts (CBCOs), while RuO_2 and PdS are valid valence band co-catalysts (VBCOs). They are proved to be beneficial for the efficient charge separation and oxidation-reduction reaction on the surface activity. However,

the reports about simultaneously combining CBCO and VBCO as dual co-catalysts with catalyst promoting the photocatalytic hydrogen evolution from water splitting are still few. In this paper, our team chooses some molybdenum compounds, MoO₂, MoS₂ and MoSe₂ as CBCOs and PdS as VBCO, to improve the photocatalytic activity of ZnS [33-42].

Here, several CBCOs (MoO₂, MoS₂ and MoSe₂) and catalyst ZnS were obtained by hydrothermal method. An up-conversion luminescence agent (Er³⁺:Y₃Al₅O₁₂) was synthesized by sol-gel method. And then, three novel visible-light photocatalysts, Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoO₂, Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoS₂ and Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoSe₂, were successfully prepared by deposition and calcination methods. Na₂S and Na₂SO₃ solution as common model sulfide pollutants was used as sacrificial agents. The photocatalytic hydrogen evolution performance of Er³⁺:Y₃Al₅O₁₂/PdS-ZnS loading with various CBCOs (MoO₂, MoS₂ and MoSe₂) were investigated. The experimental results showed that the photocatalytic hydrogen evolution activity of Er³⁺:Y₃Al₅O₁₂/PdS-ZnS could be significantly enhanced in the presence of MoX₂ (X = O, S and Se) as co-catalyst under visible light irradiation. In addition, the mechanism of up-conversion luminescence of Er³⁺:Y₃Al₅O₁₂ and the related excitation principle of Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoX₂ (X = O, S and Se) photocatalysts were proposed. These photocatalysts offer a more promising idea for the large-scale visible-light photocatalytic hydrogen evolution.

Experimental

Materials and chemicals

All the chemicals were of analytical pure and used without further purification. Erbium oxide (Er₂O₃, 99.999 %), yttrium oxide (Y₂O₃, 99.999 %) and aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, 99 %,

Sinopharm Chemical Reagent Co., Ltd, China), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5 %, Sinopharm Chemical Reagent Co., Ltd, China) and nitric acid (HNO_3 , 65 %, Veking Company, China) were used to synthesize the up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). Molybdenum disulphide (MoS_2 , 99 %, Aladdin Industrial Corporation, China), Molybdenum Trioxide (MoO_3 , 99.5 %, Shanghai Huayi Group Huayuan Chemical Industry Co., Ltd, China), Molybdenum powder (Mo, 99.5 %, Aladdin Industrial Corporation, China), Ammonium Chloride (NH_4Cl , 99.5 %, Sinopharm Chemical Reagent Co., Ltd, China), Sodium molybdate dehydrate ($\text{Na}_2\text{MoO}_6 \cdot 2\text{H}_2\text{O}$, 99 %, Sinopharm Chemical Reagent Co., Ltd, China), Selenium powder (Se, 99 %, Sinopharm Chemical Reagent Co., Ltd, China), Hydrazine hydrate ($\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$, 85 %, Sinopharm Chemical Reagent Co., Ltd, China) and palladium chloride (PdCl_2 , 99 % , Sinopharm Chemical Reagent Co., Ltd, China) were used as co-catalysts precursor. Zinc acetate dihydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$, 99 %, Sinopharm Chemical Reagent Co., Ltd, China), dodecyl sodium sulfate ($\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$, 65 %, Sinopharm Chemical Reagent Co., Ltd, China) and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98 %, Aladdin Industrial Corporation, China) were used to synthesize the nano-sized ZnS particles. Sodium sulfite anhydrous (Na_2SO_3 , 97 %, Sinopharm Chemical Reagent Co., Ltd, China) and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98 %, Sinopharm Chemical Reagent Co., Ltd, China) were dissolved with double distilled water (Millipore Corporation, USA) as sacrificial agents.

Preparation of photocatalysts

The up-conversion luminescence agent, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, was synthesized by sol-gel way [43-44]. At the beginning, $\text{Y}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ solutions were planted by dissolving 2.27 g Y_2O_3 (0.01 mol) and 0.01 g Er_2O_3 (3.34×10^{-5} mol) into appropriate hot HNO_3 solution (about 60 °C), respectively. The

planted $\text{Y}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ solutions were put together with 12.62 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.03 mol) while stirring magnetically, and the homogenous solution was acquired. Then, the 33.93 g solid citric acid (0.17 mol) was also put into the mentioned mixture solution (mol ratio of citric acid: metal ion is 3:1). The solution was continued to be stirred and heated at 50-60 °C until the transparent sol was successfully formed. And then, the sol was heated at 80 °C for 24 h and became the gel. After the gel cooled in the air, it was ground into good homogeneous powders. For the sake of removing residual organic components and nitrate ions the powders were heated at 1100 °C for 2.0 h in a muffle furnace. In the end, the sintered substance was removed and permitted to cool down to the room temperature in atmosphere. Consequently, the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ particles were obtained.

MoO_2 were prepared by a simple hydrothermal process [45,46]. 0.43 g MoO_3 (3.0 mmol) and 0.14 g Mo powder (1.5 mmol) were dispersed in 25 mL double distilled water. 100 mg NH_4Cl was added to the mixture under vigorous stirring at room temperature. The mixture was subsequently transferred into a 50 mL capacity Teflon-lined stainless steel autoclave before heated at 180 °C for 12 h. After the reaction, the autoclave was naturally cooled to room temperature. The black powder MoO_2 was obtained by centrifugation, washed three times with double distilled water and ethanol, and dried at 60 °C in a vacuum.

MoSe_2 was synthesized by a hydrothermal method [47,48]. 0.48 g Na_2MoO_4 (2.0 mmol) was dispersed in 50 mL double distilled water under continuous stirring to form a transparent solution. In a separate flask, 0.32 g Se powder (4.0 mmol) was dissolved in 10 mL hydrazine hydrate. After a period of time, 10 mL Se-hydrazine hydrate was added to Na_2MoO_4 solution slowly. The color of the obtained mixture became orange. Then the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 10 h. The black precipitate was collected by

centrifugation, washed with double distilled water. Then the product was dried at 60 °C in a vacuum. ZnS were prepared using hydrothermal method [49,50]. Firstly, 0.30 g sodium dodecylsulfate was added to the 25 mL distilled water to form a solution. 1.76 g $\text{Zn}(\text{CH}_3\text{COO})_2$ was dissolved in the above solution slowly. At this moment, the prepared $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (0.30:1.00 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and ZnS mass ratio) was also added into the above solution. Subsequently, 20 mL Na_2S (0.40 mol/L) was added dropwise to the suspension under stirring magnetically for 60 min, and then added different mass ratios of the conduction band co-catalysts (CBCOs) (MoO_2 , MoS_2 and MoSe_2). The as-formed suspension was transferred into 100 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 2.0 h. After cooling to room temperature naturally, a suspension was separated by centrifugation, washed with distilled water and ethanol three times, and then dried at 60 °C in a vacuum. The $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{ZnS}-\text{MoX}_2$ (X = O, S and Se) samples were obtained.

Modification of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{ZnS}-\text{MoX}_2$ (X = O, S and Se) with PdS (0.13 wt%) as Valence band co-catalyst (VBCO) was realized by deposition-precipitation method [51,52]. Firstly, a PdCl_2 aqueous solution (0.0011 mol/L) was added dropwise to a suspension of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{ZnS}-\text{MoX}_2$ (X = O, S and Se) powder (1.00 g, as prepared above) dispersed in Na_2S aqueous solution (0.50 mol/L) under stirring magnetically. After centrifugation, washed thoroughly with water and dried at 60 °C for 10 h. The obtained powders were calcined in vacuum at 200 °C for 3.0 h. Finally, the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS}-\text{ZnS}-\text{MoX}_2$ (X = O, S and Se) photocatalysts were acquired. For the purpose of comparison, the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS}-\text{ZnS}$ were also prepared in the same way.

Characterization of catalysts

The prepared samples were characterized by powder X-ray diffraction (XRD, D-8, Bruker-axs,

Germany), scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan), transmission electron microscopy (TEM, JEOL JEM2100, Hitachi Corporation, Japan), energy dispersive X-ray spectroscopy (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan), UV-vis absorption spectra (UV-2450, Shimadzu, Japan) and PL spectra (RF-5301PC, Shimadzu, Japan).

Photocatalytic reactions

The photocatalytic hydrogen evolution experiments were performed in a 500 mL Pyrex reactor at ambient temperature and atmospheric pressure. The headspace of the reactor was connected to an inverted burette which is filled with water, allowing the measurement of the evolved hydrogen gas. In a typical photocatalytic experiment, the prepared photocatalyst was dispersed under constant stirring in an aqueous solution containing 0.20 mol/L Na₂S and 0.30 mol/L Na₂SO₃. Before irradiation, the system was bubbled with argon for 30 min to remove the dissolved air inside in order to ensure the reaction system was under an anaerobic condition. Then, the suspensions were irradiated for 5.0 h using a 300 W xenon lamp (LX-300, Deruifeng hardware electrical appliance businesses, China) applied as light source, which was positioned on the side of photoreactor. The irradiation wavelength was controlled by a combination of a cold mirror (CM-1) and a water filter ($400\text{ nm} < \lambda < 800\text{ nm}$). For visible-light irradiation, a cut off filter (L42) was fitted to the aforementioned light source ($400 < \lambda < 800\text{ nm}$). The formation of hydrogen was confirmed by injecting 0.50 mL of the reactor headspace gas in a gas chromatograph (GC-8A, MS-5A column, TCD, Ar Carrier, Shimadzu, Japan).

Results and discussion

XRD, SEM, TEM, EDX, UV-Vis absorption and PL spectra

The as-prepared samples were first characterized by using XRD measurements. The $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (Fig. 1a) was identified according to JCPDS #33-0040 file of $\text{Y}_3\text{Al}_5\text{O}_{12}$. It demonstrated that $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ had been synthesized, in which the Er^{3+} ions entered the crystal lattice, taking the place of partial Y^{3+} ion. From Fig. 1b, it can be seen that, for the MoO_2 sample, the crystalline phase is same as JCPDS #32-0671 of standard MoO_2 , with characteristic diffraction peaks at 26.0° (011), 36.9° (111), 41.5° (120), 53.3° (112), 60.2° (031) and 66.5° (131), which are all well-defined also with the MoO_2 sample. From Fig. 1c, several diffraction peaks can also be seen at 14.4° , 32.7° , 39.6° , 44.1° , 49.8° and 60.4° , being consistent with (002), (100), (103), (104), (105) and (113) crystalline planes of MoS_2 in (JCPDS #65-3656), respectively. As for MoSe_2 (Fig. 3d), the diffraction peaks at $2\theta = 13.7^\circ$, 32.2° and 53.8° can be indexed as the (002), (100) and (106) diffraction planes of MoSe_2 (JCPDS #87-2419), respectively. From Fig. 1e, all the diffraction peaks can be indexed as those of ZnS (JCPDS #05-0566). And that, no other diffraction peaks of impurities were observed. As shown in Fig. 1(f and g), the patterns consist of two sets of diffraction peaks, which can match well with that of ZnS (Fig. 1e) and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (Fig. 1a), respectively. However, the shape and intensity of two pattern peaks are different due to the addition of PdS. Fig. 1(h, I and j) shows the characteristic peaks of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$, respectively. From Fig. 1(h, I and j), it can be seen that there are two sets of diffraction peaks belonging to ZnS and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, respectively. The diffraction peaks assigned to MoO_2 , MoS_2 , MoSe_2 and PdS could hardly be observed in the patterns, due to the tiny content and high dispersion of them. Even so, these patterns also showed that some slight changes occurred with adding them. It suggests in turn that they exist in the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($\text{X} = \text{O}, \text{S}$ and Se). In addition, the particle sizes of prepared samples were calculated based on XRD data using the Scherrer formula (1)

[53]:

$$D = K\lambda/B\cos\theta \quad (1)$$

Herein D , K , λ , B and θ represent particle size, linear dimension of particle, wave-length of incident x-rays, full width-half maximum (FWHM) and Bragg angle, respectively. Because the as-prepared samples were characterized by X-ray powder diffraction (Radiation = CuK α 1) analysis, $\lambda=1.54056$. K is a constant near unity ($K = 0.98$). By determining the average particle sizes from FWHM and θ they were calculated, from a corresponding XRD data, to be 26.0, 10.5, 9.83 and 20.8 nm for Er³⁺:Y₃Al₅O₁₂, ZnS, MoO₂ and MoO₂, respectively.

The detailed morphology, size and microstructure of the obtained samples were investigated by using SEM and TEM and the results were shown in Fig. 2 and Fig. 3, respectively. Fig. 2a shows the homogeneous sphere of Er³⁺:Y₃Al₅O₁₂ particles with average size of 30 nm. It can be seen from Fig. 2e that the pure ZnS consists of regular nanospheres with approximately 15 nm in dimensions. Fig. 2(h, I and j) shows the overall morphology of Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoX₂ ($X = O, S$ and Se) and these samples are composed of different size nanospheres, among them the size of the massive spheres is about 15 nm, confirming the ZnS nanospheres, while the surfaces of the ZnS are loaded with some small particles with diameter of 10 nm. These particles can be verified as PdS nanoparticles. Meanwhile, there are some slightly greater nanospheres which can be regarded as the Er³⁺:Y₃Al₅O₁₂ particles. It should be pointed out that, with regard to CBCOs (MoO₂, MoS₂ and MoSe₂), they are difficult to be observed because of their lower loading content and small size.

However, the existences of these CBCOs (MoO₂, MoS₂ and MoSe₂) in Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoX₂ ($X = O, S$ and Se) can be clearly identified in TEM images (Fig. 3(b, c and d)). The TEM images confirm that the spherical structures of CBCOs (MoO₂, MoS₂ and MoSe₂)

were the assemblies of numerous tiny particles (diameter < 10 nm). Fig. 3(h, I and j) shows the TEM of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($\text{X} = \text{O}, \text{S}$ and Se) composite particles. It can be seen that the ZnS displays the regular sphere shape with average diameter about 15 nm. Besides, some nanospheres with a diameter around 30 nm should be $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ particles. Particularly, PdS and MoX_2 ($\text{X} = \text{O}, \text{S}$ and Se) nanoparticles as cocatalysts are randomly dispersed on the surface of ZnS particles. The typical particle sizes of PdS and MoX_2 ($\text{X} = \text{O}, \text{S}$ and Se) are estimated to be about 10 nm and less than 5 nm, respectively. Moreover, the TEM image results of grain diameter were consistent with the above calculated results from XRD data.

The EDX results of the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($\text{X} = \text{O}, \text{S}$ and Se) are presented in Fig. 4. These images also indicate that Er, Y, Al, O, Zn, S, Pd and Mo elements are coexisting in each catalyst, which are close to the stoichiometric ratio. Besides, the EDX data (in Fig. 4) also show the existence of O, S and Se elements, respectively, for $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($\text{X} = \text{O}, \text{S}$ and Se). These results were consistent with the XRD pattern presented above simultaneously.

The UV-vis absorption and PL spectra of up-conversion luminescence agent, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, are illustrated in Fig. 5. From Fig. 5a, it can be seen that three typical absorption peaks locate at 410 nm, 524 nm and 653 nm, respectively, in absorption spectra, which indicates that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ can absorb visible-lights. Fig. 5(b, c and d) shows the PL spectra of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ under the excitation wavelengths of 410 nm, 524 nm and 653 nm, respectively. The emission peaks are conspicuous in the ultraviolet-light region (250-400 nm). Therefore, it can be confirmed that the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as up-conversion luminescence agent can absorb visible-lights and emit ultraviolet-lights. These findings forebode that the ZnS combined with $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ will be activated effectively by visible-light to enhance the effect of photocatalytic hydrogen evolution.

Influence of loaded amount of CBCOs (MoO₂, MoS₂ and MoSe₂) on visible-light photocatalytic hydrogen evolution activity

Fig. 6 illustrates the influences of the CBCOs (MoO₂, MoS₂ and MoSe₂) with different loaded amounts on the photocatalytic activity of Er³⁺:Y₃Al₅O₁₂/PdS-ZnS catalysts. It could be remarked that all of the Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoX₂ (X = O, S and Se) photocatalysts present higher photocatalytic hydrogen evolution activities than that over Er³⁺:Y₃Al₅O₁₂/PdS-ZnS, revealing that the MoX₂ (X = O, S and Se) affects the photocatalytic activity dramatically. The photocatalytic activity loading MoO₂ is slightly higher than that loading MoS₂. In photocatalytic reactions, the dispersed CBCOs (MoO₂, MoS₂ and MoSe₂) particles at an apposite concentration behaved as catalytic centres or reservoirs for excited electrons. In the process, the electrons are transferred from ZnS conduction band (CB) to the CBCOs, and the holes accumulate in the ZnS valence band (VB). Hence, the photo-generated electrons and holes could efficiently be separated. For these three CBCOs (MoO₂, MoS₂ and MoSe₂), the MoSe₂ can be considered as a most efficient CBCO, which can fast facilitate photo-generated electron transfer. In addition, the photo-generated electrons migrated from the inner region of ZnS to the surfaces can be injected into CBCOs as the active site to take part in reduction reaction (H⁺ → H₂). From Fig. 6, it can be seen that introducing suitable CBCOs (0.3 wt%) into Er³⁺:Y₃Al₅O₁₂/ZnS system displays a positive effect on the hydrogen production. Compared with 0.1 wt% loading amounts of CBCOs, apparently, more loading amounts of CBCOs (0.3 wt%) can provide more active sites to take part in hydrogen production reaction,. However, the amount of photocatalytic hydrogen production decreases slightly with further increase of CBCOs content to 0.5 wt% in Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoX₂ (X = O, S and Se). Perhaps, the further increase of CBCOs content exorbitantly covers the surface of ZnS particles, which will result in the decrease of photo-generated

electron amount. It must decrease the amount of photocatalytic hydrogen production. Therefore, the optimum loading amounts of CBCOs is a significant parameter for photocatalytic hydrogen production reaction.

Visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se)

Fig. 7 shows the comparison of hydrogen evolution amounts catalysed by $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se) along with visible-light irradiation time. All experiments were conducted in triplicate under standardized test conditions. It can be found that, obviously, the amounts of hydrogen evolution all significantly increase with the lengthening of visible-light irradiation time for four photocatalysts. However, the amounts by using $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se) are much more than that by using $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ at any visible-light irradiation time. It reveals that the presence of MoX_2 ($X=\text{O}, \text{S}$ and Se) could dramatically improve the visible-light photocatalytic hydrogen evolution activity of the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ catalyst. The results also show that the photocatalytic capability of the CBCOs is in the order of $\text{MoSe}_2 > \text{MoO}_2 > \text{MoS}_2$ with 0.3 wt% loading content.

Visible-light photocatalytic hydrogen evolution mechanism of

$\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se)

Through above experimental observations, the corresponding feasible mechanism is illustrated in Fig. 8. In Fig. 8a, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as an up-conversion luminescence agent absorbs visible-light, and then emits ultraviolet-light, which excites wide band gap photocatalyst ZnS (band gap: 3.6 eV) producing photo-generated electron/hole pairs at the same time. For the efficient separation of photo-generated

electrons and photo-generated holes, the VBCO (PdS) and CBCOs (MoO_2 , MoS_2 and MoSe_2) in the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se) composites play a dominating role, respectively. In the photocatalytic hydrogen evolution reaction, PdS as a VBCO is known to be able to transfer holes from VB, to carry out the oxidation reaction with sacrificial reagents (Na_2S and Na_2SO_3). The electrons are expected to transfer from the CB of ZnS to the CBCOs (MoO_2 , MoS_2 and MoSe_2). And then, the reduction reaction for hydrogen evolution occurs on the surface of CBCOs (MoO_2 , MoS_2 and MoSe_2). However, due to the transfer ability of electrons, the effects of CBCOs (MoO_2 , MoS_2 and MoSe_2) are not the same.

As shown in Fig. 8b, those CBCOs with narrow band-gap and relatively negative CB position (close to the property of the metal) should be beneficial to the transfer of photo-generated electrons. In general, the narrow band-gap is more benefit to secondary excitation of electron from the CB of ZnS back to the VB of CBCOs under the same condition. And that the relatively negative CB position is favorable to the reduction reaction of hydrogen ions forming H_2 . In regard to these CBCOs (MoO_2 , MoS_2 and MoSe_2), MoO_2 has the most negative CB, which is closest to the CB of ZnS. However, the band-gap of MoO_2 is the widest among these three COCBs, which goes against the secondary excitation of photo-generated electron. MoSe_2 has the relatively negative CB and narrowest band-gap, while MoS_2 has neither narrow band-gap nor relatively negative CB. Taking all into account, the capability of electron transfer is in the order of $\text{MoSe}_2 > \text{MoO}_2 > \text{MoS}_2$.

On the basis of the above analysis, it can be believed that these reasons lead to the enhanced activity of ZnS photocatalyst.

Conclusions

In this work, an up-conversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$) and several conduction band co-catalysts (CBCOs) (MoO_2 , MoS_2 and MoSe_2) were fabricated via simple sol-gel and hydrothermal methods, respectively. And then, three visible-light photocatalysts, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$, were successfully prepared by deposition and calcination methods. Research results showed that, when these molybdenum compounds (MoO_2 , MoS_2 and MoSe_2) were used as CBCOs, the visible-light photocatalytic hydrogen evolution performance of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ was significantly enhanced. It is attributed to the promotions of CBCOs (MoO_2 , MoS_2 and MoSe_2) and VBCO (PdS) on the transfer of photo-generated electrons and holes, respectively, consuming Na_2S and Na_2SO_3 as sacrificial reagents to produce hydrogen. The common usage of CBCOs (MoO_2 , MoS_2 and MoSe_2) and VBCO (PdS) inhibits the recombination of electrons and holes, enhancing the performance of photocatalytic hydrogen evolution. Comparing with these CBCOs (MoO_2 , MoS_2 and MoSe_2), the MoSe_2 is more in favor of the transfer of photo-generated electrons due to the narrow band-gap and relatively negative CB position. Furthermore, the MoSe_2 , as ideal CBCOs, can also be used to modify other photocatalysts to enhance the visible-light photocatalytic hydrogen evolution performance.

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Fig. 1. The XRD patterns of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, (b) MoO_2 , (c) MoS_2 , (d) MoSe_2 , (e) ZnS , (f) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{ZnS}$, (g) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$, (h) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, (i) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and (j) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$.

Fig. 2. The SEM images of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, (e) ZnS , (h) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, (i) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and (j) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$.

Fig. 3. The TEM images of (b) MoO_2 , (c) MoS_2 , (d) MoSe_2 , (h) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, (i) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and (j) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$.

Fig. 4. The EDX patterns of (h) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, (i) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and (j) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$.

Fig. 5. UV-Vis absorption spectrum (a) and PL spectra (b-d) of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$.

Fig. 6. Influence of loaded amount of CBCOs (MoO_2 , MoS_2 and MoSe_2) on visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$.

Fig. 7. Visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se).

Fig. 8. The schematic diagram of (a) charge transfer process and (b) band structure in $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($X = \text{O}, \text{S}$ and Se) for visible-light photocatalytic hydrogen evolution.

Figures:

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Fig. 2. The SEM images of (a) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, (e) ZnS , (h) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, (i) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and (j) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$.

Fig. 3. The TEM images of (b) MoO₂, (c) MoS₂, (d) MoSe₂, (h) Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoO₂, (i) Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoS₂ and (j) Er³⁺:Y₃Al₅O₁₂/PdS-ZnS-MoSe₂.

Fig. 4. The EDX patterns of (h) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoO}_2$, (i) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoS}_2$ and (j) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$.

Fig. 5. UV-Vis absorption spectrum (a) and PL spectra (b-d) of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$.

Fig. 6. Influence of loaded amount of CBCOs (MoO₂, MoS₂ and MoSe₂) on visible-light photocatalytic hydrogen evolution activity of Er³⁺:Y₃Al₅O₁₂/PdS-ZnS.

Fig. 7. Visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoX}_2$ ($\text{X} = \text{O}, \text{S}$ and Se).

Fig. 8. The schematic diagram of (a) charge transfer process and (b) band structure in $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS}-\text{ZnS}-\text{MoX}_2$ ($X = \text{O}, \text{S}$ and Se) for visible-light photocatalytic hydrogen evolution.

Graphical abstract

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Articles

Enhanced visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ by conduction band co-catalysts (MoO_2 , MoS_2 and MoSe_2)

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Several conduction band co-catalysts (CBCOs), MoO_2 , MoS_2 and MoSe_2 , were prepared to improve the visible-light photocatalytic hydrogen evolution activity of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS}$ from water splitting. The visible-light photocatalytic hydrogen evolution activity of the prepared photocatalysts was evaluated by using Na_2S and Na_2SO_3 as sacrificial reagents in an aqueous solution under visible light irradiation. $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{PdS-ZnS-MoSe}_2$ with 0.30 wt% MoSe_2 shows the highest visible-light photocatalytic hydrogen evolution activity.