Efficient photocatalytic hydrogen evolution from methanol/water splitting over $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles under infrared-visible light irradiation

Yang Chen, Chunxiao Lu, Liang Tang, Shengnan Wei, Yahui Song, Jun Wang*

College of Chemistry, Liaoning University, Shenyang 110036, P.R. China

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ABSTRACT

In this paper, two efficient up-conversion luminescence agents, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (from infrared light to ultraviolet light) and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (from visible light to ultraviolet light), were synthesized by hydrothermal and sol-gel methods, respectively. And then, a novel photocatalyst, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles, were successfully prepared by hydrothermal and calcination methods for infrared-visible light photocatalytic hydrogen evolution. For comparison and confirmation, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{MoS}_2\text{-NaTaO}_3$, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$, and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ were all characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The photocatalytic activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles was examined through photocatalytic hydrogen evolution from methanol splitting under infrared-visible light irradiation. The influence factors such as mass ratio of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and NaTaO_3 , calcination temperature, solution acidity (pH) and

* Corresponding author. Tel.: +86-24-62207861; Fax: +86-24-62202053.
E-mail address: wangjun888tg@126.com (J. Wang).

used time on the infrared-visible light photocatalytic hydrogen evolution activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles were studied. Particularly, the prepared $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles with the mass ratio of 0.3:1.0 heat-treated at 500 °C for 120 min in pH = 6.0 solution with 10.0 wt % methanol displayed a high infrared-visible light photocatalytic activity in hydrogen production from water solution.

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* Corresponding author. Tel.: +86-24-62207861; Fax: +86-24-62202053.

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In this paper, two efficient up-conversion luminescence agents, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (from infrared light to ultraviolet light) and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (from visible light to ultraviolet light), were synthesized by hydrothermal and sol-gel methods, respectively. And then, a novel photocatalyst, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles, were successfully prepared by hydrothermal and calcination methods for infrared-visible light photocatalytic hydrogen evolution. For comparison and confirmation, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{MoS}_2\text{-NaTaO}_3$, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$, and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ were all characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The photocatalytic activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles was examined through photocatalytic hydrogen evolution from methanol splitting under infrared-visible light irradiation. The influence factors such as mass ratio of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and NaTaO_3 , calcination temperature and solution acidity (pH) and used time on the infrared-visible light photocatalytic hydrogen evolution activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles were studied. Particularly, the prepared $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles with the mass ratio of 0.3:1.0 heat-treated at 500 °C for 120 min in pH = 6.0 solution with 10.0 wt % methanol displayed a high infrared-visible light photocatalytic activity in hydrogen production from water solution.

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1. Introduction

With the increasingly serious issue of energy crisis and environmental pollution, it is the importantly urgent task to explore the renewable energy. In recent years, hydrogen (H_2) has been identified as one of most potential energy because it is not only a higher energy yield, but also pollution-free and such benefit as easily stored at the same time [1-3]. Since the pioneer Fujishima and Honda reported on photoelectrochemical water splitting on a TiO_2 electrode [4,5], the photocatalytic

water splitting to produce hydrogen has become a very promising way. This method should be the most renewable, applicable and promising choice for the production of hydrogen [6-8].

The up-conversion luminescence agent can generate one high-energy photon by absorbing two or several incident low-energy photons. And the previous works have proved that combining with the up-conversion luminescence agent can effectively enhance the activity of semiconductor in photocatalytic water splitting to produce hydrogen [9-15]. However, the single up-conversion luminescence agent can hardly match well with the bandwidth of photocatalyst. The absorption and emission spectra of rare earth ions come mainly from the electronic transition of inner 4f electron orbits. In the periphery of 5s and 5p electronic shielding, the 4f electronic orbits hardly interacts with the outer substrates. Thus, the absorption and emission spectra of doped rare earth ions are similar to those of free rare earth ions, showing a very sharp peaks and resulting in the low efficiency of photocatalytic water splitting to produce hydrogen. It was reported that the $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ can transform near-infrared photons to ultraviolet and visible photons, which is considered as one of the most efficient up-conversion luminescence material [16-18]. And another up-conversion luminescence agent, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, can transform visible light to the ultraviolet light widely used in many fields due to its high up-conversion luminescence efficiency and stability [19-21]. Considering these deficiencies of the up-conversion luminescence materials, we first propose to use two kinds of up-conversion luminescence agents to expand the the absorption and emission range.

It has been reported that the NaTaO_3 , a highly efficient photocatalyst, has been studied because of its outstanding performance in photocatalytic splitting water to produce hydrogen [22]. However, because the band-gap of NaTaO_3 is 4.0 eV, it only can be activated by the ultraviolet-lights to perform the photocatalytic hydrogen production reaction. Unfortunately, the ultraviolet-lights only account for

4.0 % in solar energy [23-27]. Therefore, in this paper we combine the NaTaO₃ with two up-conversion luminescence agents, Er³⁺:Y₃Al₅O₁₂ and Tm³⁺,Yb³⁺:NaYF₄, to enhance the photocatalytic activity of NaTaO₃. In other words, in order to sufficiently employ the visible light (~ 48 %) and near-infrared light (~ 44 %) in solar light, we simultaneously select the infrared-ultraviolet up-conversion Tm³⁺,Yb³⁺:NaYF₄ and visible-ultraviolet up-conversion Er³⁺:Y₃Al₅O₁₂ to combine with wide energy band-gap NaTaO₃ photocatalysts for fully utilizing the solar light.

In this paper, two effective up-conversion luminescence agents, Tm³⁺,Yb³⁺:NaYF₄ (from infrared to ultraviolet) and Er³⁺:Y₃Al₅O₁₂ (from visible to ultraviolet), were synthesized by hydrothermal and sol-gel methods, respectively. The nano-sized NaTaO₃ particles were also obtained by hydrothermal method. And then, as an infrared-visible light photocatalyst, the Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ nanocomposites were successfully prepared by direct mixing and calcination methods. The experimental results displayed that the infrared-visible light photocatalytic hydrogen production activity of NaTaO₃ can be significantly enhanced by using Tm³⁺,Yb³⁺:NaYF₄, Er³⁺:Y₃Al₅O₁₂ and MoS₂. Besides, the up-conversion luminescence mechanisms of Tm³⁺,Yb³⁺:NaYF₄ and Er³⁺:Y₃Al₅O₁₂ and the possible infrared-visible light photocatalytic hydrogen production process of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ under infrared-visible light irradiation were also proposed.

2. Experimental procedure

2.1. Materials and reagents

Thulium oxide (Y₂O₃, 99.999 %), ytterbium oxide (Yb₂O₃, 99.999 %), hydrochloric acid (HCl), ammonium fluoride (NH₄F), ethylene glycol (C₂H₆O₂), sodium chloride (NaCl) and

polyvinylpyrrolidone (PVP K-30) (Veking Company, China) were used to synthesize the up-conversion luminescence agents ($\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). Ta_2O_5 (99.99 % impurity, Aldrich, USA) and NaOH (99.5 %, Sinopharm Chemical Reagent Co. Ltd, China) were used to prepare the photocatalyst (NaTaO_3). Molybdenum sulfide (MoS_2 , 98 %, Sinopharm Chemical Reagent Co, Ltd, China) was used as co-catalyst precursor for preparing $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles [28,29]. Double distilled water (Millipore Corporation, USA) was mixed with methanol (Veking Company, China), which was acted as sacrificial agent, to prepare the reaction solutions. All chemicals were used without further purification.

2.2. Syntheses of up-conversion luminescence agents ($\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$)

The up-conversion luminescence agent, $\beta\text{-Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, was prepared by a solvothermal process [17]. First of all, the stoichiometric rare earth oxides Y_2O_3 , Yb_2O_3 and Tm_2O_3 were dissolved into appropriate HCl solution with a stoichiometric ratio of 79.5: 20: 0.5 to obtain the YCl_3 , YbCl_3 and TmCl_3 solutions. The mixtures were heated under continuous stirring to completely evaporate the water. The obtained rare earth (RE) chlorides were dissolved in a certain amount of ethylene glycol (EG) under vigorous stirring at the temperature of 60 °C. After adding the PVP and NaCl, the temperature of the solution was controlled at 80 °C to form a homogeneous solution under continuous stirring. In addition, a certain amount of NH_4F was dissolved into EG and they were added slowly to the solution mentioned above under continuous stirring until forming a transparent solution. The obtained precursor was transferred to a 50 mL autoclave (stainless steel Teflon-lined). The autoclave

was maintained at 180 °C for 12 h, cooling down to room temperature under natural conditions. Finally, the formed samples were filtered, washed and then dried to obtain the $\beta\text{-Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$.

The $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ was synthesized by the sol-gel and calcination methods [30]. First of all, in order to obtain the $\text{Y}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ solutions, 0.5679 g Y_2O_3 and 0.0032 g Er_2O_3 were dissolved into appropriate hot HNO_3 solution (about 60 °C), respectively. The obtained $\text{Y}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ solutions were mixed with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ under continuous stirring until the homogenous solution was obtained. Then the solid citric acid was added into the above solution (mol ratio of citric acid: metal ion is 3:1). The remaining solution was stirred and heated around 50-60 °C to prepare the transparent sol. Afterward, the sol was heated at 80 °C until the gel was formed, which was well ground into homogeneous powders. Subsequently, the powders were calcined at 1200 °C for 2.0 hours in muffle furnace to remove residual organic components and nitrate ions. At last, after cooling down to the room temperature naturally, the sintered substance was taken out of the muffle furnace. Finally, the desired white particles of $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ were obtained.

2.3. Preparation of NaTaO_3 as photocatalyst

The pure NaTaO_3 photocatalyst was obtained under mild hydrothermal condition [31]. The NaOH and Ta_2O_5 (Ta/Na molar ratio of 1:10) were added to 25 mL deionized water. After stirring the suspension in the water bath at 80 °C for 2.0 hours and then was transferred to a 50 mL Teflon-lined stainless steel autoclave, maintained at 180 °C for 12 hours. After cooling down to room temperature naturally, the obtained suspension was filtered, washed and dried to obtain the sodium tantalate (NaTaO_3) nanoparticles.

2.4. Preparation of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$,

Tm³⁺,Yb³⁺:NaYF₄/MoS₂-NaTaO₃ and Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃

The Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ nanocomposite particles were prepared through the ultrasonic dispersion and liquid boiling methods [32]. The Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂ (the molar ratio of Tm³⁺,Yb³⁺:NaYF₄ and Er³⁺:Y₃Al₅O₁₂ was controlled at 1:1) and NaTaO₃ powders (the mass ratio of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂ and NaTaO₃ was adopted 0.3:1.0) were added into a 200 mL beaker filled with 30 mL deionized water and then fully dispersed by ultrasound (frequency: 80 kHz and output power: 50 W) for 30 min. The suspended liquid was boiled for a period of time until the water evaporated. Subsequently, the obtained sample was filtrated, washed and calcined at 500 °C for 120 min in a muffle furnace at the calefactive rate of 2.0 °C·min⁻¹. Then the Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/NaTaO₃ catalysts were obtained after fully grinding.

The MoS₂ as cocatalyst was modified on the surface of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/NaTaO₃ particles by ultrasonic dispersion and liquid boiling method to improve the infrared-visible light photocatalytic hydrogen evolution activity of the Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/NaTaO₃ nanocomposite particles [33]. For the preparation of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ photocatalyst, 1.00 g Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/NaTaO₃ nanocomposite particles were put in 200 mL of ethanol, and 0.2 wt % commercial MoS₂ powder was added, adequately dispersed by ultrasound (frequency: 80 kHz and output power: 50 W) for 30 min. The suspended liquid was boiled until the water evaporated. Subsequently, the obtained sample was filtrated, washed and heated in a constant temperature oven and then the temperature was controlled at 180 °C for 60 min. Finally, after grinding the Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃, infrared-visible light photocatalysts, was obtained.

The $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ photocatalysts were also prepared in a similar manner in accordance with the above mentioned preparation steps. Adding the $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, the photocatalyst $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ was prepared and the adding the $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, the photocatalyst $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ was prepared.

2.5. Analytical methods

The prepared samples were characterized by powder X-ray diffraction (XRD, D-8, Bruker-axs, Germany) using Ni filtered Cu $K\alpha$ radiation in the range of 2θ from 10° to 70° , scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan) and energy dispersive X-ray spectroscopy (EDX, JEOL JSM-5610LV, Hitachi Corporation, Japan).

2.6. Infrared-visible light photocatalytic hydrogen evolution experiments

the experiment for photocatalytic water splitting for hydrogen production under infrared-visible light radiations were conducted in a 500 mL Pyrex reactor. The headspace of the reactor connected with an inverted burette to measure the produced hydrogen gas was filled with methanol-water solution at atmospheric pressure. In the reactions of photocatalytic splitting water for hydrogen production, a needed amount (280 mg) of photocatalysts, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$, were dispersed in methanol-water solution (10.0 wt %) under continuous stirring. After purging the suspensions by argon flow for 30 min at least to wipe out dissolved air, the suspensions were irradiated for 5.0 h using a 300 W xenon lamp (400-1200 nm) (Microsolar 300, Beijing perfectlight science and technology Ltd, China). The produced hydrogen was confirmed by the gas chromatograph (GC-8A, MS-5A column, TCD, Ar Carrier, Shimadzu, Japan).

3. Results and discussion

3.1. XRD, SEM and EDX of $Tm^{3+}, Yb^{3+}:NaYF_4$, $Er^{3+}:Y_3Al_5O_{12}$, $MoS_2-NaTaO_3$,

$Tm^{3+}, Yb^{3+}:NaYF_4/MoS_2-NaTaO_3$, $Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ and

$Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$

Fig. 1 shows the XRD patterns of prepared $Tm^{3+}, Yb^{3+}:NaYF_4$ (a), $Er^{3+}:Y_3Al_5O_{12}$ (b), $NaTaO_3$ (c), $MoS_2-NaTaO_3$ (d), $Tm^{3+}, Yb^{3+}:NaYF_4/MoS_2-NaTaO_3$ (e), $Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ (f) and $Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ (g). Obviously, the XRD pattern of synthesized $Tm^{3+}, Yb^{3+}:NaYF_4$ (Fig. 1 (a)) and $Er^{3+}:Y_3Al_5O_{12}$ (Fig. 1 (b)) are remarkably similar to the JCPDS #16-0334 file of $NaYF_4$ [34] and JCPDS #33-0040 file of $Y_3Al_5O_{12}$ [35], respectively. It is demonstrated that the $Tm^{3+}, Yb^{3+}:NaYF_4$ and $Er^{3+}:Y_3Al_5O_{12}$ have been successfully obtained through the above-mentioned synthesis methods. In Fig. 1 (c), from these obvious characteristic diffraction peaks at $2\theta = 22.85^\circ$ (100), $2\theta = 32.55^\circ$ (110), $2\theta = 40.23^\circ$ (111), $2\theta = 46.67^\circ$ (200) and $2\theta = 52.58^\circ$ (210), the crystal phase of prepared $NaTaO_3$ nanoparticles can be judged to be a pure perovskite structure, according to the standard card (JCPDS # 74-2478) [36]. Compared with the characteristic diffraction peaks of $NaTaO_3$ in Fig. 1 (c), there is an extra diffraction signal at the location of 14.4° (002) in Fig. 1 (d), which should accord with the crystal signal of MoS_2 (powder diffraction file (PDF) # 771716). From Fig. 1 (d-g), it can be seen that the main characteristic diffraction peaks of perovskite structural $NaTaO_3$ all exist. In addition, it can also be found that the diffraction peaks of $Tm^{3+}, Yb^{3+}:NaYF_4$ in Fig. 1 (e and g) and the diffraction peaks of $Er^{3+}:Y_3Al_5O_{12}$ in Fig. 1 (f and g) all exist, which indicates that the $Tm^{3+}, Yb^{3+}:NaYF_4/MoS_2-NaTaO_3$ (e), $Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ (f) and $Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ (g) nanocomposite particles have been

successfully prepared. All these diffraction peaks of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ (e), $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (f) and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (g) hardly shift, compared with their respective peaks of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, MoS_2 and NaTaO_3 , which displays that the crystal conformations of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ are not changed in the combination. And yet the intensities of all diffraction peaks of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ in $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ powder weakens obviously as against that of pure $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ powders. Hence, the crystal forms of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ composites can be identified as mixed crystal phase of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, MoS_2 and NaTaO_3 .

Fig. 1.

The SEM images of the prepared $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (a), $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (b), $\text{MoS}_2\text{-NaTaO}_3$ (c), $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ (d), $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (e) and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (f) are all given in Fig. 2. From the image of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ depicted in Fig. 2 (a), many hexagonal particles with 50-60 nm particle size can be seen clearly. As seen in Fig. 2 (b), the irregular spherical particles with 40-50 nm particle size can be found clearly. And in Fig. 2 (c), there are mainly cube-like crystal particles with a size of about 200 nm, which belong to the typical crystal form of NaTaO_3 . In addition, a lot of morphology homogeneous gray elliptic balls with a size of about 50 nm attached to the surface of cube-like crystal

NaTaO₃ particles. It proves that the MoS₂ tiny particles have been deposited on the surface of NaTaO₃ nanoparticles. In comparison, in Fig. 2 (d-f) the Tm³⁺,Yb³⁺:NaYF₄/MoS₂-NaTaO₃ (d), Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ (e) and Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ (f) catalysts display an anomalous form with the same average size as that of the MoS₂-NaTaO₃ particles. Particularly, it can be seen that there are many small hexagonal or spherical particles on the surface of cube-like crystal NaTaO₃ particles. Besides, many small white flake particles on the surface of cube-like crystal particles can also be found. These findings prove that the Tm³⁺,Yb³⁺:NaYF₄, Er³⁺:Y₃Al₅O₁₂ and mixed Tm³⁺,Yb³⁺:NaYF₄ and Er³⁺:Y₃Al₅O₁₂ have been combined with NaTaO₃ and the MoS₂ has also been deposited on the surface of them.

Fig. 2.

The EDX spectra of synthesized Tm³⁺,Yb³⁺:NaYF₄ (a) and Er³⁺:Y₃Al₅O₁₂ (b) nanoparticles and prepared MoS₂-NaTaO₃ (c) nanoparticles and Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ (d) nanocomposite particles are all shown in Fig. 3. As displayed in Fig. 3 (a), the synthesized Tm³⁺,Yb³⁺:NaYF₄ is composed of stoichiometric Na, Y, F, Yb and light Tm (the atomic percentage of Na, Y and F was estimated to be 23.12 %, 13.45 % and 60 %). The quantification of Na, Y and F confirmed that the atomic ratio of Na: Y: F was 1.00: 0.80: 4.00, which closely agrees with the stoichiometric composition of NaYF₄. As displayed in Fig. 3 (b), the results of EDX give the peaks of Er, Y, Al, and O elements, which demonstrates the composition of Er³⁺:Y₃Al₅O₁₂ up-conversion luminescence agent. Besides, the atomic ratio of synthesized Er³⁺:Y₃Al₅O₁₂ up-conversion luminescence agent is the same with the atomic ratio given in the Fig. 3 (b). From Fig. 3 (c) it can be seen that the MoS₂-NaTaO₃ catalysts are composed of Mo, S, Na, Ta and O elements. In addition, the

prepared $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ catalyst contains MoS_2 , NaTaO_3 , $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (see Fig. 3 (d)), the ratio of each material in the catalysts is similar as that of the precursor solution. And these results are consistent with the XRD patterns presented above as well.

Fig. 3.

3.2. Photocatalytic activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$,

$\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{MoS}_2\text{-NaTaO}_3$ in infrared-visible light photocatalytic hydrogen evolution

Fig. 4 shows the relation between the hydrogen evolution amounts generated from $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{MoS}_2\text{-NaTaO}_3$ photocatalysts and the infrared-visible light irradiation time. It can be found that the hydrogen evolution amounts all increase gradually with the lengthening of infrared-visible light irradiation time for all photocatalysts. And the hydrogen evolution amounts by using $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles are much more than that of $\text{MoS}_2\text{-NaTaO}_3$ nanoparticles at any infrared-visible light irradiation time. Obviously, it can be considered that, because of the presence of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ possessing up-conversion luminescence effect from near-infrared light and visible light to ultraviolet light, the $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ can provide more ultraviolet-lights to stimulate the wide energy band-gap NaTaO_3 to carry out effective infrared-visible light photocatalytic hydrogen evolution. Compared these photocatalytic hydrogen evolution amounts catalyzed by

$\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$, it can be found that the $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ as photocatalyst shows the most obvious advantage. That is, the coexistence of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ as up-conversion luminescence agents can more effectively enhance the infrared-visible light photocatalytic hydrogen evolution activity of the $\text{MoS}_2\text{-NaTaO}_3$ photocatalyst.

Fig. 4.

3.3. Influence of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and NaTaO_3 mass ratio on infrared-visible light photocatalytic hydrogen evolution activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$

Fig. 5. shows the relationship between the photocatalytic hydrogen evolution amounts of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles and the molar ratios of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ under infrared-visible light irradiation. It can be seen that the amount of infrared-visible light photocatalytic hydrogen production increases at first along with the increase of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ content (from 0.0:1.0 mass ratio to 0.3:1.0 mass ratio), and then slightly falls with further increase of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ content (from 0.3:1.0 mass ratio to 0.5:1.0 mass ratio). It indicates that the $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and NaTaO_3 mass ratio can markedly affect the infrared-visible light photocatalytic hydrogen production activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$. The appropriate increase of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ content can offer much more ultraviolet-light to activate the wide energy band-gap NaTaO_3 through up-conversion luminescence from visible light and infrared light to

ultraviolet-light. Therefore, it can cause the increase of the total amount of infrared-visible light photocatalytic hydrogen production. However, because of using direct mixing method, the further increase of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ content may relatively decrease the active surface of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ photocatalyst particles. Thus, it leads to the decrease of the volume of infrared-visible light photocatalytic hydrogen production.

Fig. 5.

3.4. Influence of calcination temperature on infrared-visible light photocatalytic hydrogen evolution activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$

Generally speaking, the effect of calcination temperature on the activity of many catalysts is obviously evident. From Fig. 6, it can be found that a low yield of infrared-visible light photocatalytic hydrogen production appears at calcination temperature of 300 °C for both $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{MoS}_2\text{-NaTaO}_3$. This illuminates that the low calcination temperature is adverse to the combination among $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, MoS_2 and NaTaO_3 . And that, at 500 °C calcination temperature a high yield of infrared-visible light photocatalytic hydrogen production is jointly attained for two used catalysts. Moreover, when the calcination temperature is up to 700 °C, the amounts of infrared-visible light photocatalytic hydrogen productions of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ and $\text{MoS}_2\text{-NaTaO}_3$ are both less than their corresponding ones at 500 °C. Apparently, at appropriate calcination temperature the NaTaO_3 particles can form the large specific surface area, generating more active sites at the surface to facilitate the redox reaction [37]. When the calcination temperature is too high, the catalyst particles would agglomerate to form large large size particles, which would decrease the photocatalytic activity.

In summary, the photocatalytic hydrogen production activity of $\text{MoS}_2\text{-NaTaO}_3$ and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ is similar at low calcination temperature. When the calcination temperature is increased, the photocatalytic hydrogen production activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ becomes higher than that of $\text{MoS}_2\text{-NaTaO}_3$.

Fig. 6.

3.5. Effect of solution acidity (pH) on infrared-visible light photocatalytic hydrogen

production of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$

In general, the solution acidity (pH) can affect the efficiency of photocatalytic hydrogen production from water splitting for any catalyst. Therefore, in this section the effect of solution acidity (pH) was studied in the pH = 4.0-10.0 range under infrared-visible light irradiation. In Fig. 7 it can be found that the amount of infrared-visible light photocatalytic hydrogen production increases at first with the increase of methanol solution pH value, and then decreases slightly along with the further increase solution pH value. Obviously, at pH = 6.0, the amount of infrared-visible light photocatalytic hydrogen production reaches a maximum. The experimental phenomena illustrates that weak acidic or neutral conditions are conducive to photocatalytic H_2 evolution in the case of methanol utilized as sacrifice agent, whereas strong acidic or basic conditions are unfavorable [38]. Perhaps, too many hydrogen ions (H^+) corrode the surface of catalyst particles, decreasing the active sites. On the contrary, strong basic conditions can not provide enough the hydrogen ions (H^+) forming hydrogen (H_2).

Fig. 7.

3.6. Infrared-visible light photocatalytic hydrogen evolution stability of

For photocatalytic hydrogen evolution from water splitting, long term and recycling usages of catalysts are necessary. In this section, the cyclic photocatalytic hydrogen evolution experiments are carried out under the same conditions to investigate the stability of $Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$. As shown in Fig. 8, the infrared-visible light photocatalytic hydrogen evolution amount decreases only slightly with the increase of used time. It indicates that the $Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ as hydrogen evolution photocatalyst remains a relative good activity in four cycles. It can be judged that this photocatalyst is basically stable in this system.

Fig. 8.

3.7. Possible up-conversion luminescence process and infrared-visible light photocatalytic hydrogen evolution mechanism of $Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$

Recently, some research groups have reported the luminescent characteristics of ultraviolet-light up-conversion luminescence in $Tm^{3+}, Yb^{3+}:NaYF_4$ and $Er^{3+}:Y_3Al_5O_{12}$ crystals, and the up-conversion luminescence mechanisms in detail. When the $\beta-Tm^{3+}, Yb^{3+}:NaYF_4$ is irradiated by a 980 nm laser beam, the emission signals at 288 nm, 360 nm and 345 nm are observed and assigned to the transitions of $^1I_6 \rightarrow ^3H_6$, $^2D_1 \rightarrow ^3H_6$ and $^1I_6 \rightarrow ^3F_4$ [40,41], respectively. Besides, the emission signals at 350 nm and 361 nm are also found by a 976 nm laser excitation and assigned to the transitions $^3P_0 \rightarrow ^3F_4$ and $^1D_2 \rightarrow ^3H_6$ [42], respectively. Apparently, the $Tm^{3+}, Yb^{3+}:NaYF_4$ can effectively absorb near-infrared photons and then emit ultraviolet light because the Yb^{3+} ion has a large absorption cross section from 970 nm to 1000 nm [43,44]. For $Er^{3+}:Y_3Al_5O_{12}$ acting as a visible-ultraviolet up-conversion

luminescence agent, when it is pumped by a 488 nm laser, the up-conversion signals of 271 nm, 317 nm and 381 nm can be observed. And the up-conversion signal at 320 nm is also found by a 647 nm laser excitation. The corresponding literatures have given the up-conversion fluorescence spectra and energy-level diagrams displaying related transitions [17,39]. According to the energy level data given in references, the up-conversion signals of 271 nm, 317 nm and 381 nm are assigned to the transitions of $^2H_{9/2} \rightarrow ^4I_{15/2}$, $^2P_{3/2} \rightarrow ^4I_{15/2}$ and $^4G_{11/2} \rightarrow ^4I_{15/2}$, respectively. The sun lights contain the continuous pump wavelengths including near-infrared light and visible light sections. Thus, if the sun lights are used as excitation source, these up-conversion process may easily take place in $Tm^{3+}, Yb^{3+}:NaYF_4$ and $Er^{3+}:Y_3Al_5O_{12}$ crystals. Therefore, using a combination of $Tm^{3+}, Yb^{3+}:NaYF_4$ and $Er^{3+}:Y_3Al_5O_{12}$ up-conversion luminescence agents can greatly improve the wide energy band-gap semiconductor photocatalysts in the sunlight utilization.

The mechanism of photocatalytic hydrogen evolution from methanol/water splitting caused by $Tm^{3+}, Yb^{3+}:NaYF_4-Er^{3+}:Y_3Al_5O_{12}/MoS_2-NaTaO_3$ nanocomposite particles under infrared-visible light irradiation is shown in Fig. 9. The influence on photocatalytic H_2 evolution is complicated. In general, the efficiency of photocatalytic H_2 evolution may be connected to following several reasons, (a) the levels of the valence band (VB) and conduction band (CB) of photocatalysts in regard to those of redox couples in solution, (b) the change of photocatalyst surface, (c) distributions of molecular and dissociative species in methanol solution and (d) competitive adsorption of molecular and dissociative species of methanol on photocatalyst surface. As the infrared-ultraviolet and visible-ultraviolet up-conversion luminescence agents, the $Tm^{3+}, Yb^{3+}:NaYF_4$ and $Er^{3+}:Y_3Al_5O_{12}$ absorb the near-infrared and visible solar lights, respectively, and then both emit the high-energy ultraviolet lights, which can effectively activate the $NaTaO_3$ nanoparticles to perform photocatalytic reaction. Under the irradiation

of ultraviolet light emitted by $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$, the photogenerated-electrons (e^-) from valence-band (VB) of NaTaO_3 leap to the conduction-band (CB), creating photogenerated-holes (h^+) in the valence-band (VB) at the same time. And the previous studies showed that the photogenerated-electrons in the conduction-band (CB) of NaTaO_3 nanocrystal could be injected into MoS_2 nanoparticles as co-catalyst [45]. The MoS_2 deposited on the surface of NaTaO_3 nanocrystal can not only accept electrons acting as active sites for hydrogen production, but also restrain the recombination rate of photogenerated-electrons (e^-) and photogenerated-holes (h^+). Apparently, it can enhance the photocatalytic activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ photocatalysts. Due to the high reducibility, the photogenerated-electrons (e^-) can reduce the H^+ cations in the water to produce H_2 . At the same time, the photogenerated-holes (h^+) with highly oxidability on valence-band (VB) of NaTaO_3 can oxidize the methanol as sacrificial agent to methanal or methanoic acid. In addition, considering the stability of photocatalysts and relatively sufficient hydrogen ions (H^+), the weak acidic and neutral conditions should be conducive to photocatalytic H_2 evolution in the case of methanol utilized as sacrifice agent [46].

4. Conclusions

In this study, two effective up-conversion luminescence agents, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (from infrared light to ultraviolet light) and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (from visible light to ultraviolet light), were synthesized. And then, for infrared-visible light photocatalytic hydrogen evolution the corresponding infrared-visible light photocatalyst ($\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$) was prepared. According to the experimental results, we can conclude that the activity of photocatalytic splitting water to produce hydrogen of NaTaO_3 can be immensely enhanced by these two up-conversion

luminescence agents ($\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). Also, the photocatalytic activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ is higher than that of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ and $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$. Further more, the photocatalytic hydrogen evolution activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ is related to the mass ratio of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$, calcination temperature and initial solution pH value. For given experimental parameter, the prepared photocatalyst, $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$, with the condition of 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio and 0.2 wt % MoS_2 at 500 °C content calcination temperature for 120 min in aqueous methanol solution with initial pH = 6.0 display a highest infrared-visible light photocatalytic hydrogen evolution activity.

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References

- [1] K. He, M. Wang, L.J. Guo, Novel-CdS-nanorod with stacking fault structures: Preparation and properties of visible-light-driven photocatalytic hydrogen production from water, *Chem. Eng. J.* 279 (2015) 747-756.
- [2] J. Xu, X.J. Cao, Characterization and mechanism of MoS_2/CdS composite photocatalyst used for

- hydrogen production from water splitting under visible light, *Chem. Eng. J.* 560 (2015) 624-648.
- [3] Y. Yan, F.P. Cai, Y. Song, W.D. Shi, InVO₄ nanocrystal photocatalysts: Microwave-assisted synthesis and size-dependent activities of hydrogen production from water splitting under visible light, *Chem. Eng. J.* 233 (2013) 1-7.
- [4] H.S. Kim, D.J. Kim, B.S. Kwak, G.B. Han, M.H. Um, M. Kang, Synthesis of magnetically separable core@shell structured NiFe₂O₄@TiO₂ nanomaterial and its use for photocatalytic hydrogen production by methanol/water splitting, *Chem. Eng. J.* 243 (2014) 272-279.
- [5] W.Q. Cui, S.S. Ma, L. Liu, Y.H. Liang, PbS-sensitized K₂Ti₄O₉ composite: Preparation and photocatalytic properties for hydrogen evolution under visible light irradiation, *Chem. Eng. J.* 204-206 (2014) 1-7.
- [6] J.S. Jang, H.G. Kim, J.S. Lee. Heterojunction semiconductors: A strategy to develop efficient photocatalytic materials for visible light water splitting, *Catal. Today* 185 (2012) 270-277.
- [7] K. Lalitha, R.J. Krishna, S.M.V. Phanikrishna, V.D. Kumari, M. Subrahmanyam, Continuous hydrogen production activity over finely dispersed Ag₂O/TiO₂ catalysts from methanol:water mixtures under solar irradiation: A structure-activity correlation, *Int. J. Hydrog. Energy* 35 (2010) 3991-4001.
- [8] B.S. Huang, F.Y. Chang, M.Y. Wey, Photocatalytic properties of redox-treated Pt/TiO₂ photocatalysts for H₂ production from an aqueous methanol solution, *Int. J. Hydrog. Energy* 35 (2010) 7699-7705.
- [9] S.G. Li, Y.W. Guo, L. Zhang, J. Wang, Y. Li, Y. Li, B.X. Wang, Visible-light photocatalytic activity of Pt supported TiO₂ combined with up-conversion luminescence agent (Er³⁺:Y₃Al₅O₁₂) for hydrogen production from aqueous methanol solution, *J. Power Sources* 15 (2014) 21-27.
- [10] C.X. Lu, Y. Chen, Y. Li, C.H. Ma, H.B. Zhang, Y.W. Guo, J. Wang, An effective quaternary nano-sized Er³⁺:Y₃Al₅O₁₂/Pt-PdS/ZnS visible-light photocatalyst for H₂ production, *RSC Adv.* 5 (2015) 54769-54776.
- [11] H.B. Zhang, C.H. Ma, Y. Li, Y. Chen, C.X. Lu, J. Wang, Sol-gel-hydrothermal synthesis of Er³⁺:Y₃Al₅O₁₂/Pt-TiO₂ membrane and visible-light driving photocatalytic hydrogen evolution from pollutants, *Appl. Catal. A* 503 (2015) 209-217.
- [12] C.H. Ma, Y. Li, H.B. Zhang, Y. Chen, C.X. Lu, J. Wang, Photocatalytic hydrogen evolution with simultaneous photocatalytic reforming of biomass by Er³⁺:YAlO₃/Pt-TiO₂ membranes under visible light driving, *Chem. Eng. J.* 273 (2015) 277-285.
- [13] Y.W. Guo, Y. Li, S.G. Li, L. Zhang, Y. Li, J. Wang, Enhancement of visible-light photocatalytic activity of

- Pt supported potassium niobate (Pt-KNbO₃) by up-conversion luminescence agent (Er³⁺:Y₃Al₅O₁₂) for hydrogen evolution from aqueous methanol solution, *Energy* 82 (2015) 72-79.
- [14] Y. Li, Y.W. Guo, S.G. Li, Y. Li, J. Wang, Efficient visible-light photocatalytic hydrogen evolution over platinum supported titanium dioxide nanocomposites coating up-conversion luminescence agent (Er³⁺:Y₃Al₅O₁₂/Pt-TiO₂), *Int. J. Hydrog. Energy* 40 (2015) 2132-2140.
- [15] Y. Li, S.G. Li, Y. Li, Y.W. Guo, J. Wang, Visible-light driven photocatalyst (Er³⁺:YAlO₃/Pt-NaTaO₃) for hydrogen production from water splitting, *Int. J. Hydrog. Energy* 39 (2014) 17608-17616.
- [16] J.G. Tao, W.P. Qin, J. Zhou, Copper-mediated trifluoromethylation of 5-iodotriazole with (trifluoromethyl)trimethylsilane promoted by silver carbonate, *J. Fluorine Chem.* 156 (2013) 177-182.
- [17] W. Wang, W.J. Huang, Y. Ni, C.H. Lu, Z.Z. Xu, Different upconversion properties of β-NaYF₄:Yb³⁺,Tm³⁺/Er³⁺ in affecting the near-infrared-driven photocatalytic activity of high-reactive TiO₂, *ACS Appl. Mater. Interfaces* 6 (2014) 340-348.
- [18] H. Chen, Y.B. Lang, D. Zhao, C.F. He, W.P. Qin, Enhanced high-order upconversion luminescence of hexagonal phase NaYF₄:Yb³⁺,Tm³⁺ crystals coated with homogeneous shell, *J. Fluorine Chem.* 174 (2015) 70-74.
- [19] H.Y. Zhu, X. Chen, Z.F. Zheng, X.B. Ke, E. Jaatinen, J.C. Zhao, Mechanism of supported gold nanoparticles as photocatalysts under ultraviolet and visible light irradiation, *Chem. Commun.* 45 (2009) 7524-7526.
- [20] R. Dholam, N. Patel, M. Adami, A. Miotello, Physically and chemically synthesized TiO₂ composite thin films for hydrogen production by photocatalytic water splitting, *Int. J. Hydrog. Energy* 33 (2008) 6896-6903.
- [21] J. Wang, R. Li, Z. Zhang, W. Sun, R. Xu, Y. Xie, Z. Xing, X. Zhang, n-Dodecane reforming over nickel-based monolith catalysts: Deactivation and carbon deposition, *Appl. Catal. A* 334 (2008) 227-233.
- [22] H. Kato, A. Kudo, Water splitting into H₂ and O₂ on alkali tantalate photocatalysts ATaO₃ (A = Li, Na, and K), *J. Phys. Chem. B* 105 (19) (2001) 4285-4292.
- [23] X.X. Yao, T.Y. Liu, X.H. Liu, L.D. Lu, Loading of CdS nanoparticles on the (1 0 1) surface of elongated TiO₂ nanocrystals for efficient visible-light photocatalytic hydrogen evolution from water splitting, *Chem. Eng. J.* 255 (2014) 28-39.
- [24] X. Chen, S. Shen, L. Guo, S.S. Mao, Semiconductor-based photocatalytic hydrogen generation, *Chem.*

Rev. 110 (2010) 6503-6570.

- [25] S. Oros-Ruiz, R. Zanella, S.E. Collins, A. Hernández-Gordillo, R. Gómez, Photocatalytic hydrogen production by Au-MxO_y (Mdouble bond; length as m-dashAg, Cu, Ni) catalysts supported on TiO₂, Catal. Commun. 47 (2014) 1-6.
- [26] A.F. Alkaim, T.A. Kandiel, F.H. Hussein, R. Dillert, D.W. Bahnemann, Solvent-free hydrothermal synthesis of anatase TiO₂ nanoparticles with enhanced photocatalytic hydrogen production activity, Appl. Catal. A 466 (2013) 32-37.
- [27] S.H. Liu, H.R. Syu, One-step fabrication of N-doped mesoporous TiO₂ nanoparticles by self-assembly for photocatalytic water splitting under visible light, Appl. Energy 100 (2012) 148-154.
- [28] C.G. Silva, R. Juárez, T. Marino, R. Molinari, H. García, 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. 133 (2011) 595-602.
- [29] Y.H. Pai, S.Y. Fang, Preparation and characterization of porous Nb₂O₅ photocatalysts with CuO, NiO and Pt cocatalyst for hydrogen production by light-induced water splitting, J. Power Sources 230 (2013) 321-326.
- [30] J.C. Boyer, F. Vetrone, L.A. Cuccia, J.A. Capobianco, Synthesis of colloidal upconverting NaYF₄ nanocrystals doped with Er³⁺, Yb³⁺ and Tm³⁺, Yb³⁺ via thermal decomposition of lanthanide trifluoroacetate precursors, J. Am. Chem. Soc. 128 (2006) 7444-7445.
- [31] J.W. Liu, G. Chen, Z.H. Li, Z.G. Zhang, Hydrothermal synthesis and photocatalytic properties of ATaO₃ and ANbO₃ (A = Na and K), Int. J. Hydrogen Energy 32 (2007) 2269-2272.
- [32] B. Mitu, S. Vizireanu, R. Birjega, M. Dinescu, S. Somacescu, P. Osiceanu, V. Pârvulescu, G. Dinescu, Comparative properties of ternary oxides of ZrO₂-TiO₂-Y₂O₃ obtained by laser ablation, magnetron sputtering and sol-gel techniques, Thin Solid Films 515 (2007) 6484-6488.
- [33] X. Zong, H.J. Yan, G.P. Wu, G.J. Ma, F.Y. Wen, L. Wang, C. Li, Enhancement of photocatalytic H₂ evolution on CdS by loading MoS₂ as cocatalyst under visible light irradiation, J. Am. Chem. Soc. 130 (2008) 7176-7177.
- [34] L. Liang, Y. Liu, C. Bu, K. Guo, W. Sun, N. Huang, T. Peng, B. Sebo, M. Pan, W. Liu, S. Guo, X. Z. Zhao, Highly uniform, bifunctional core/double-shell-structured β-NaYF₄:Er³⁺,Yb³⁺@SiO₂@TiO₂ hexagonal sub-microprisms for high-performance dye sensitized solar cells, Adv. Mater. 25 (2013) 2174-2180.

- [35] L.N. Yin, J.G. Gao, J. Wang, B.X. Wang, R.Z. Jiang, K. Li, Y. Li, X.D. Zhang, Enhancement of sonocatalytic performance of TiO_2 by coating $\text{Er}^{3+}:\text{YAlO}_3$ in azo dye degradation, *Sep. Purif. Technol.* 81 (2011) 94-100.
- [36] S.B. Zhu, H.B. Fu, S.C. Zhang, L.W. Zhang, Y.F. Zhu, Two-step synthesis of a novel visible-light-driven $\text{K}_2\text{Ta}_2\text{O}_{6-x}\text{N}_x$ catalyst for the pollutant decomposition, *J. Photochem. Photobiol. A* 193 (2008) 33-41.
- [37] V.M. Daskalaki, D.I. Kondarides, Efficient production of hydrogen by photo-induced reforming of glycerol at ambient conditions, *Catal. Today* 144 (2009) 75-80.
- [38] L. Diamandescu, M. Feder, D. Tarabasanu-Mihaila, F. Vasiliu, Hydrothermal synthesis and structural characterisation of $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ mixed oxide nanoparticles, *Appl. Catal. A* 325 (2) (2007) 270-275.
- [39] NN. Zua, H.G. Yang, Z.W. Dai, Different processes responsible for blue pumped, ultraviolet and violet luminescence in high-concentrated $\text{Er}^{3+}:\text{YAG}$ and low-concentrated $\text{Er}^{3+}:\text{YAP}$ crystals, *Physica. B* 403 (2008) 174-177.
- [40] M. Lidija, L. Vesna, A.M. Bojan, D.D. Miroslav, M. Olivera, Hydrothermal synthesis of nanostructured Y_2O_3 and $(\text{Y}_{0.75}\text{Gd}_{0.25})_2\text{O}_3$ based phosphors, *Opt. Mater.* 35 (2013) 1817-1823.
- [41] T. Jiang, W.P. Qin, J. Zhou, Citric acid-assisted phase controlled synthesis of $\text{NaYF}_4:\text{Yb}^{3+}, \text{TM}^{3+}$ crystals and their intense ultraviolet upconversion emissions, *J. Fluorine Chem.* 156 (2013) 177-182.
- [42] C.H. Li, F. Wang, J. Zhua, J. C. Yu, $\text{NaYF}_4:\text{Yb}, \text{TM}/\text{CdS}$ composite as a novel near-infrared-driven photocatalyst, *Appl. Catal. B* 100 (2010) 433-439.
- [43] G. Boulon, A. Collombet, A. Brenier, M.T. Cohen-Adad, A. Yoshikawa, K. Lebbou, J.H. Lee, T. Fukuda, Structural and spectroscopic characterization of nominal $\text{Yb}^{3+}:\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$ oxyapatite single crystal fibers grown by the micro-pulling-down method, *Adv. Funct. Mater.* 11 (2001) 263-270.
- [44] R. Martin-Rodriguez, R. Valiente, S. Polizzi, M. Bettinelli, A. Speghini, F. Piccinelli, Upconversion luminescence in nanocrystals of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ doped with $\text{Tb}^{3+}-\text{Yb}^{3+}$ and $\text{Eu}^{3+}-\text{Yb}^{3+}$, *J. Phys. Chem. C* 113 (2009) 12195-12200.
- [45] D.R. Liu, Y.S. Jiang, G.M. Gao, Photocatalytic degradation of an azo dye using N-doped NaTaO_3 synthesized by one-step hydrothermal process, *Chemosphere* 83 (2011) 1546-1552.
- [46] Daskalaki VM, Kondarides DI. Efficient production of hydrogen by photo-induced reforming of glycerol at ambient conditions. *Catal Today* 2009;144:75-80.

Content of Figures:

Fig. 1. XRD patterns of (a) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (heat-treated at 80 °C for 12 h), (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (heat-treated at 1100 °C for 120 min), (c) NaTaO_3 (heat-treated at 500 °C for 120 min), (d) $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min), (e) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min), (f) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) and (g) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min).

Fig. 2. SEM images of (a) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (heat-treated at 80 °C for 12 h), (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (heat-treated at 1100 °C for 120 min), (c) $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min), (d) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min), (e) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) and (f) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min).

Fig. 3. EDX spectra of (a) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (heat-treated at 80 °C for 12 h), (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (heat-treated at 1100 °C for 120 min), (c) $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min) and (d) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min).

Fig. 4. Photocatalytic activities of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min), $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min), $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) and $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min) nanocomposites in infrared-visible light photocatalytic hydrogen evolution.

Fig. 5. Influence of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratios on infrared-visible light photocatalytic hydrogen production activity of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min) under infrared-visible light irradiation. (Er:YAG: $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$)

Fig. 6. Influences of calcination temperature on infrared-visible light photocatalytic hydrogen evolution activities of $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min) and $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite powders (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) under infrared-visible light irradiation. (Er:YAG: $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$)

Fig. 7. Influences of solution acidity (pH) on infrared-visible light photocatalytic hydrogen production of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) under infrared-visible light irradiation.

Fig. 8. Recycled photocatalytic hydrogen production of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) under infrared-visible light irradiation.

Fig. 9. Infrared-visible light photocatalytic hydrogen evolution principle and process of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles under infrared-visible light irradiation.

Figures:

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Fig. 2. SEM images of (a) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (heat-treated at 80 °C for 12 h), (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (heat-treated at 1100 °C for 120 min), (c) $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min), (d) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min), (e) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) and (f) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min).

Fig. 3. EDX spectra of (a) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4$ (heat-treated at 80 °C for 12 h), (b) $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (heat-treated at 1100 °C for 120 min), (c) $\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content heat-treated at 500 °C for 120 min) and (d) $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min).

Fig. 4. Photocatalytic activities of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ (0.2 wt % MoS₂ content and 0.3:1.0 Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂ and MoS₂-NaTaO₃ mass ratio heat-treated at 500 °C for 120 min), Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ (0.2 wt % MoS₂ content and 0.3:1.0 Er³⁺:Y₃Al₅O₁₂ and MoS₂-NaTaO₃ mass ratio heat-treated at 500 °C for 120 min), Tm³⁺,Yb³⁺:NaYF₄/MoS₂-NaTaO₃ (0.2 wt % MoS₂ content and 0.3:1.0 Tm³⁺,Yb³⁺:NaYF₄ and MoS₂-NaTaO₃ mass ratio heat-treated at 500 °C for 120 min) and MoS₂-NaTaO₃ (0.2 wt % MoS₂ content heat-treated at 500 °C for 120 min) nanocomposites in infrared-visible light photocatalytic hydrogen evolution.

Fig. 5. Influence of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂ and MoS₂-NaTaO₃ mass ratios on infrared-visible light photocatalytic hydrogen production activity of Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ (0.2 wt % MoS₂ content heat-treated at 500 °C for 120 min) under infrared-visible light irradiation. (Er:YAG: Er³⁺:Y₃Al₅O₁₂)

Fig. 6. Influences of calcination temperature on infrared-visible light photocatalytic hydrogen evolution activities of MoS₂-NaTaO₃ (0.2 wt % MoS₂ content heat-treated at 500 °C for 120 min) and Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂/MoS₂-NaTaO₃ nanocomposite powders (0.2 wt % MoS₂ content and 0.3:1.0 Tm³⁺,Yb³⁺:NaYF₄-Er³⁺:Y₃Al₅O₁₂ and MoS₂-NaTaO₃ mass ratio heat-treated at 500 °C for 120 min) under infrared-visible light irradiation. (Er:YAG: Er³⁺:Y₃Al₅O₁₂)

Fig. 7. Influences of solution acidity (pH) on infrared-visible light photocatalytic hydrogen production of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) under infrared-visible light irradiation.

Fig. 8. Recycled photocatalytic hydrogen production of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles (0.2 wt % MoS_2 content and 0.3:1.0 $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{MoS}_2\text{-NaTaO}_3$ mass ratio heat-treated at 500 °C for 120 min) under infrared-visible light irradiation.

Fig. 9. Infrared-visible light photocatalytic hydrogen evolution principle and process of $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles under infrared-visible light irradiation.

Graphical Abstract

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Articles

Efficient photocatalytic hydrogen evolution from methanol/water splitting over $\text{Tm}^{3+}, \text{Yb}^{3+}:\text{NaYF}_4\text{-Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}/\text{MoS}_2\text{-NaTaO}_3$ nanocomposite particles under infrared-visible light irradiation

Yang Chen, Chunxiao Lu, Liang Tang, Shengnan Wei, Yahui Song, Jun Wang*

College of Chemistry, Liaoning University, Shenyang 110036, P.R. China

Received December 2015; E-mail: wangjun888tg@126.com.