



# Highly efficient visible-light driven photocatalytic hydrogen evolution over $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$ nanocomposite

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## ABSTRACT

Here, a novel coated composite,  $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$ , was successfully prepared by sol-hydrothermal and calcination methods, in which the  $\text{MoSe}_2$  and reduced graphene oxide (rGO) hybrids as co-catalysts were used to act as the electron collector and active reaction sites.  $\text{Er}^{3+}:\text{YAlO}_3$ ,  $\text{MoSe}_2/\text{rGO}$ ,  $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5$  and  $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$  were all characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), Raman spectrum, UV–vis diffuse reflectance spectra (DRS) and transmission electron microscopy (TEM). UV–vis absorption and photoluminescence (PL) spectra of  $\text{Er}^{3+}:\text{YAlO}_3$  were also measured. The photocatalytic hydrogen production activity of  $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$  was examined under visible-light irradiation. The main influence factors such as initial solution pH and mass ratio of  $\text{Ta}_2\text{O}_5$  and  $\text{MoSe}_2/\text{rGO}$  on visible-light photocatalytic hydrogen production activity of  $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$  were discussed in detail. The results showed that the coated composite ( $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$ ) with 99.25:0.75 mass ratio of  $\text{Ta}_2\text{O}_5$  and  $\text{MoSe}_2/\text{rGO}$  in methanol aqueous solution at pH = 6.00 could display the highest photocatalytic hydrogen production activity. Furthermore, a high level of photocatalytic activity can be still maintained within five cycles under the same conditions. It implies that the novel coated composite,  $\text{Er}^{3+}:\text{YAlO}_3/\text{Ta}_2\text{O}_5/\text{rGO}/\text{MoSe}_2$ , may be a promising photocatalyst utilizing solar energy for hydrogen production.

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## 1. Introduction

In the nowadays world, the consumption of non-renewable fossil fuels has generated series of environmental concerns, and then seriously influenced on human life. Therefore, the development of the alternative energy sources has already become very urgent [1–5]. In recent years, hydrogen energy, due to the characteristics of cleaning and non-pollution, will play a key role in the energy structure [6,7]. Because the solar-light and water are abundant and free in the earth, the solar-light photocatalytic splitting water for hydrogen production will be a best choice. Since the pioneers, Fujishima and Honda, reported on photoelectrochemical splitting water on  $\text{TiO}_2$  electrode, there have been increasing semiconductor materials for photocatalytic splitting water to produce hydrogen investigated by many researchers in the world [8–12]. Especially, many inorganic oxide materials, owing to its low energy consumption in preparation, large surface area and high adsorption, have caught people's interests. In these materials, the

tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) due to its outstanding performance has been utilized in photocatalytic hydrogen production field [13–18]. Particularly,  $\text{Ta}_2\text{O}_5$  has wide band-gap ( $E_{\text{bg}} = 3.90$  eV) [19,20], enough hydrogen production power and high photocatalysis velocity, so it displays a fairly high photocatalytic efficiency in hydrogen production under corresponding ultraviolet-light irradiation.

Nevertheless, owing to so wide band-gap, the  $\text{Ta}_2\text{O}_5$  only can be activated by ultraviolet-light which accounts for about 4.0% in solar-light [21,22]. Recently, concerning this issue, some rare earth compounds with up-conversion luminescent function, which can generate one high-energy photon by absorbing two or more low-energy photons, have been applied in photocatalytic reaction to improve the photocatalytic hydrogen production activity of wide band-gap semiconductor materials [23–26]. In previous work, we reported that the use of  $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$  as up-conversion luminescence agent could dramatically enhance the visible-light photocatalytic hydrogen production activity of  $\text{TiO}_2$ . Therefore, in this work, we adopted the wide band-gap  $\text{Ta}_2\text{O}_5$  to combine with a new up-conversion luminescence agent,  $\text{Er}^{3+}:\text{YAlO}_3$ , to enhance the visible-light photocatalytic hydrogen production activity of  $\text{Ta}_2\text{O}_5$ . In this designed catalytic system,  $\text{Er}^{3+}:\text{YAlO}_3$  can effectively transform visible-lights into ultraviolet-lights to satisfy the energy

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requirement for wide band-gap Ta<sub>2</sub>O<sub>5</sub>. Obviously, it may increase the utilization ratio for solar energy. In addition, in previous researches the direct mixing method was employed to prepare the Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/Pt-TiO<sub>2</sub> as visible-light photocatalyst [27]. It may well relatively decrease the active surface of TiO<sub>2</sub> particles and then lose the hydrogen production ability. So, in the present work we selected the sol-gel method to prepare a coated Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> coated composite as visible-light photocatalyst, which would efficiently carry out the photocatalytic hydrogen production from water splitting.

Furthermore, as well known, the photogenerated electrons and holes in semiconductor photocatalyst have a high recombination rate, which may greatly decrease the catalytic activity. Fortunately, recent researches manifested that the co-catalyst could play a significant role in dealing with this problem. According to previous study, depositing Pt on the surface of Ta<sub>2</sub>O<sub>5</sub> particles can restrict the recombination of photogenerated electron-hole pairs, enhancing the photocatalytic hydrogen production activity of Ta<sub>2</sub>O<sub>5</sub> [28]. However, Pt is a rare and noble metal, so its large-scale applications are limited. Apparently, it is necessary to find some appropriate co-catalysts to replace Pt. They also can effectively restrict the electron-hole recombination to enhance the photocatalytic hydrogen evolution activity of Ta<sub>2</sub>O<sub>5</sub>. Recently, the graphene, due to the superior electro-conductivity, special surface, high adsorption and two-dimensional nature, was considered to be an effective substance to restrict the electron-hole recombination in traditional semiconductor photocatalysts [29–31]. The graphene can act as an electron-transfer bridge and quickly transfer electrons from conduction band (CB) to other places. Thus, the graphene as co-catalyst has been applied in photocatalytic hydrogen production [32–34], while the reports on the combination of graphene with Ta<sub>2</sub>O<sub>5</sub> are still very few [35]. In this work, we selected the graphene to combine with Ta<sub>2</sub>O<sub>5</sub> through a certain design technology, which employed the good conductivity of graphene, fastly transferring the electrons from conduction (CB) band of Ta<sub>2</sub>O<sub>5</sub> to the surface of graphene and reducing the H<sup>+</sup> to produce H<sub>2</sub>. In addition, in order to further improve the photocatalytic activity of Ta<sub>2</sub>O<sub>5</sub>, the MoSe<sub>2</sub> was also added into co-catalyst system. MoS<sub>2</sub> is an excellent traditional co-catalyst and can vastly enhance the photocatalytic hydrogen evolution activity of some common photocatalysts. Compared to MoS<sub>2</sub>, MoSe<sub>2</sub> has much lower electric potential and higher electrical conductivity as well as the coverage rate of hydrogen on the edge [36,37]. So, the MoSe<sub>2</sub> as co-catalyst can not only more effectively resist the photogenerated electron-hole recombination, but act as the active sites reducing H<sup>+</sup> to produce hydrogen (H<sub>2</sub>). And that, it has already been proved that the MoSe<sub>2</sub> can be used for photocatalytic hydrogen production [38–40]. Hence, in this study, we prepared the Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> coated composite on sheet MoSe<sub>2</sub>-reduced graphene oxide (MoSe<sub>2</sub>-rGO) for further enhancing the photocatalytic hydrogen production activity of Ta<sub>2</sub>O<sub>5</sub>.

In this work, the synthesis of Er<sup>3+</sup>:YAlO<sub>3</sub> as up-conversion luminescence agent by using sol-gel process and preparation of Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> coated composite and Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub>/rGO/MoSe<sub>2</sub> visible-light photocatalyst by using sol-hydrothermal and calcination methods were reported. The composition, morphologies and photocatalytic performance of the prepared samples were investigated and the mechanism of visible-light photocatalytic splitting methanol/water to produce hydrogen was also proposed. The experimental results showed that the photocatalytic hydrogen production performance of Ta<sub>2</sub>O<sub>5</sub> could be significantly enhanced in the presence of Er<sup>3+</sup>:YAlO<sub>3</sub> and MoSe<sub>2</sub>/rGO under visible-light irradiation. It is wished that this study would provide some valuable strategies for photocatalytic hydrogen production using solar energy in the future.

## 2. Experimental

### 2.1. Materials and reagents

Erbium oxide (Er<sub>2</sub>O<sub>3</sub>, 99.999% purity), Yttrium oxide (Y<sub>2</sub>O<sub>3</sub>, 99.999% purity) and Aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, analytical

reagent), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, analytical reagent) and nitric acid (HNO<sub>3</sub>, 65%, analytical reagent) (Veking Company, China) were used to synthesize the up-conversion luminescence agent (Er<sup>3+</sup>:YAlO<sub>3</sub>). Tantalum pentachloride (TaCl<sub>5</sub>, 99.99%, analytical reagent) and absolute ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, analytical reagent) (Veking Company, China) were used to prepare the Ta<sub>2</sub>O<sub>5</sub>. Hydrazine hydrate (H<sub>4</sub>N<sub>2</sub>·xH<sub>2</sub>O, analytical reagent), Sodium molybdate dehydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, analytical reagent), Selenium powder (Se, analytical reagent) and Graphene oxide (Veking Company, China) were used to prepare the co-catalyst (MoSe<sub>2</sub>/rGO). Double distilled water (Millipore Corporation, USA) was buffered with methanol (CH<sub>3</sub>OH, analytical reagent, Veking Company, China), which was used to act as sacrificial agent. All chemicals were analytical grade and used without further purification.

### 2.2. Preparation of catalysts

#### 2.2.1. Synthesis of Er<sup>3+</sup>:YAlO<sub>3</sub> as up-conversion luminescence agent

According to the previous reports, the Er<sup>3+</sup>:YAlO<sub>3</sub> as up-conversion luminescence agent was synthesized by sol-gel and calcination methods [23,24]. Firstly, by dissolving stoichiometric Y<sub>2</sub>O<sub>3</sub> (5.4562 g) and Er<sub>2</sub>O<sub>3</sub> (0.0938 g) into 50 mL hot HNO<sub>3</sub> solution (about 60 °C) the Y(NO<sub>3</sub>)<sub>3</sub> and Er(NO<sub>3</sub>)<sub>3</sub> mixed solutions were prepared. Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (9.1000 g) powder was mixed with the prepared Y(NO<sub>3</sub>)<sub>3</sub> and Er(NO<sub>3</sub>)<sub>3</sub> solutions under magnetically stirring at room temperature. After stirring for 30 min, the homogenous solution of Y(NO<sub>3</sub>)<sub>3</sub>, Er(NO<sub>3</sub>)<sub>3</sub> and Al(NO<sub>3</sub>)<sub>3</sub> was obtained. The solid citric acid powder was added in batches into the above mixture solution according to 3:1 mol ratio of citric acid and metal ions (Y<sup>3+</sup>, Er<sup>3+</sup> and Al<sup>3+</sup>). The mixture solution was further magnetically stirred and then heated at 50–60 °C until the transparent sol successfully formed. The transparent sol was heated at 80 °C for 24.0 h until became the gel. After being naturally cooled to room temperature in the air, the gel was adequately ground into fine homogeneous powders. Subsequently, for completely removing the residual organic components and nitrate ions the homogeneous powders were calcined at 1100 °C for 2.0 h. The sintered substance was taken out of the muffle furnace and allowed to cool down to the room temperature in atmosphere. At last, the desired white Er<sup>3+</sup>:YAlO<sub>3</sub> powder as up-conversion luminescence agent was obtained after fully grinding.

#### 2.2.2. Preparation of Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> coated composite as photocatalyst

The Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> coated composite was prepared by sol-gel process. At first, the transparent TaCl<sub>5</sub> solution was obtained by dissolving the required amount of TaCl<sub>5</sub> in absolute alcohol, then adding the Er<sup>3+</sup>:YAlO<sub>3</sub>. The citric acid as chelating agent of Ta<sup>5+</sup> ions, in which

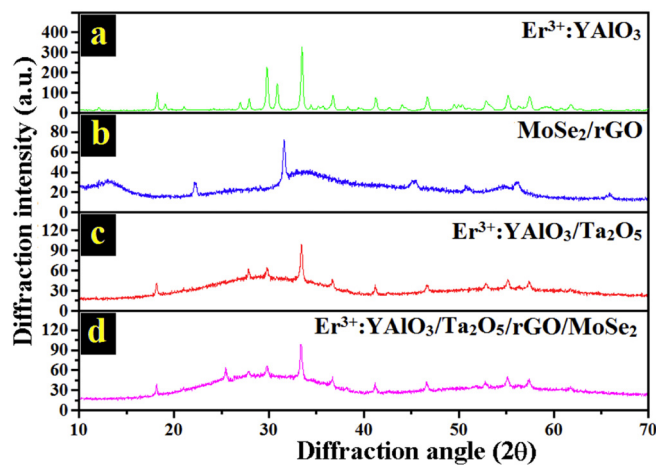


Fig. 1. XRD patterns of prepared Er<sup>3+</sup>:YAlO<sub>3</sub> (a), MoSe<sub>2</sub>/rGO (b), Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> coated composite (c) and Er<sup>3+</sup>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub>/rGO/MoSe<sub>2</sub> composite (99.25:0.75 mass ratio of Ta<sub>2</sub>O<sub>5</sub> to MoSe<sub>2</sub>/rGO) (d).

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