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Sol–gel-hydrothermal synthesis of Er^{3+}:$Y_3Al_5O_{12}$/Pt–TiO_2 membrane and visible-light driving photocatalytic hydrogen evolution from pollutants

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ABSTRACT

A novel visible-light photocatalyst, Er^{3+}:$Y_3Al_5O_{12}$/Pt–TiO_2 membrane, was prepared via sol–gel–hydrothermal method on glass substrates as a support. X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) were used to reveal the crystallinity, surface morphology and chemical composition of the prepared Er^{3+}:$Y_3Al_5O_{12}$/Pt–TiO_2 membrane. The catalytic activity of Er^{3+}:$Y_3Al_5O_{12}$/Pt–TiO_2 membrane was examined through the photocatalytic hydrogen evolution from some pollutants, including phenol, glycerol and Na_2S/Na_2SO_3, which were used as electron donors, under visible-light irradiation. Furthermore, some influence factors, such as mass ratio, pre-treatment temperature and used times, on the photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}$/Pt–TiO_2 membrane were studied. The experimental results showed that the Er^{3+}:$Y_3Al_5O_{12}$/Pt–TiO_2 membrane is a good and broad-spectrum photocatalyst in visible-light photocatalytic hydrogen evolution with simultaneous pollutant solution treatment.

1. Introduction

Nowadays, with the fossil fuel resource decreasing and the serious environmental pollution caused by fossil fuel combustion, new, clean and sustainable sources of energy attracts more and more attention. The solar energy is one of the most promising energy due to its free, easily accessible and inexhaustible characteristics. Hydrogen, an attractive alternative clean energy, is expected to become a major energy source in the future [1]. Sequentially, most researchers attempt to convert solar energy to hydrogen [2,3]. Hydrogen is currently produced from a variety of primary sources, such as natural gas, naphtha, heavy oil, methanol, biomass, wastes, coal, wind energy, hydropower and nuclear energy [4–6]. Considering the energy and environmental issues, the production of hydrogen must use the renewable resources (like water) and renewable energy sources (like solar energy) [7]. Therefore, the solar-light photocatalytic water splitting to produce hydrogen has been considered as one of the most potential method, because it is a simple and environmentally friendly process, utilizing the clean and abundant resources of water and solar energy [8–11]. The process is also thought to be an ideal method to solve the problems of environmental pollution and energy crisis [12]. However, at current state the efficiency of photocatalytic hydrogen generation is very low because of the lack of a satisfactory electron donor. Many researches have involved some sacrificial agents as electron donors, such as methanol, formic acid and EDTA [13–18]. In fact, these electron donors are also useful chemical products. A convenient choice from the environmental and economic standpoints is combining hydrogen production with synthesis of useful chemicals or recovery of contaminated wastewater [19,20], which is also a path that has been recently explored [21]. Wastewater derived from dye industry, printing and dyeing industry, leather industry and paper making industrial often contains Na_2S. If this wastewater was directly discharged to the nature, the health of human and nature would be threatened. Phenol wastewaters refer those permanent organic pollutants containing phenolic compounds produced from coking, oil refining, papermaking, plastics, ceramics and textiles industries. Also, they are high toxic substances. The danger of wastewater containing phenolic compounds on the natural environment and human health is very serious and not easy to remove. Glycerol is widely used in the life, industry and medicine, thus, it is a common emission organic pollutant. Even though it has not a strong toxicity, uncontrolled release of wastewater including glycerol may create the increase of the environment's load and the environment serious worsening. In fact, the degradation of pollutants alone is also a waste of resources. Therefore, we try to use

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glycerol, phenol and Na_2S/Na_2SO_3 as sacrificial agent to study the performance of photocatalyst in photocatalytic hydrogen evolution under visible-light driving. This not only demonstrate the feasibility of producing hydrogen from pollution solution through the photocatalytic process, but also degrades pollutants effectively, achieving the dual purpose of environmental remediation and energy production. It will provide a practical and lowcost technology in the hydrogen-based energy system.

Usually, there are two key factors on high efficiency of photocatalytic hydrogen production from pollutants in the practical hydrogen-based energy system. One is to develop a photocatalyst that can work efficiently under solar-light irradiation. Another is the photocatalyst can be easily separated from water and reused effectively. Various kinds of semiconductors to photocatalytic reaction have gained increasing attention of researchers around the world [22–24]. Among various semiconductors, titanium dioxide (TiO_2) has been still considered as the most promising material and extensively application due to its inexpensiveness, high physical and chemical stability, non-toxicity, and excellent photocatalytic activity [25,26]. However, it is still far from being a perfect and ideal photocatalyst. The main disadvantage of TiO_2 is that it is active only under ultravoilet-light due to its wide band gap ($E_{bg} = 3.2$ eV) [27]. Nevertheless, the ultravoilet-light in solar spectrum is less than 5.0%. In order to obtain a photocatalyst being capable of responding to visible-light, we have been engaged in the research of TiO_2 combined with some up-conversion luminescence agents to perform the simulated visible-light photocatalytic degradation of pollutants and achieved some satisfactory results in the past few years [28–32]. The high degradation effect can be attributed to some special properties of the up-conversion luminescence agents, which can generate one high-energy photon by absorbing two or more incident low-energy photons. As well known, some up-conversion luminescence agents, such as $NaYF_4$:Yb/Er, $CaSc_2O_4$:Yb/Er, $Er^{3+}:YAlO_3$ and $Er^{3+}:Y_3Al_5O_{12}$, have been studied detailedly [33,34]. Among them, the $Er^{3+}:Y_3Al_5O_{12}$ has been widely used in many fields due to its high conversion luminescence efficiency and chemical stability. Therefore, in this article we are trying to use the $Er^{3+}:Y_3Al_5O_{12}$ as an effective up-conversion luminescence agent from visible-light to ultraviolet-light combined with TiO_2 to obtain a novel $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ photocatalyst to perform the visible-light photocatalytic hydrogen evolution with simultaneous pollutants degradation.

In addition, to retard the recombination rate of photogenerated electrons (e^-) and holes (h^+), noble metal (e.g., Pt, Ru) or metal oxide (e.g., NiO, RuO_2) as a co-catalyst are introduced to load on the surface of photocatalyst [35–36]. Nevertheless, suspended $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ powder generally present some insurmountable shortcomings. The $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ particles in suspension are too difficult to be removed from aqueous phase. It is harmful to regeneration and recycle of catalysts [37,38]. Furthermore, the catalyst particles may become a cause of turbidity in the drainage as a secondary pollutant. Some researches have carried out to support TiO_2 on some substrate materials as thin membranes or membranes by sol–gel methed. However, there are some disadvantages for film including their uneven, bad cycle reversibility and stability, therefore great efforts have been made in order to improve or modify their property. In the present work, we designed a novel methed, which combined the conventional sol–gel procss with hydrothermal to synthesize the $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane on the glass substrate. The prepared $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane has high degree of crystallization, high stability, and narrow particle size distribution [39–43]. Moreover, the membrane can be easily separated from water and are advantageous to regenerate and recycle, which has a great potential in photocatalytic hydrogen evolution and pollutant treatment using solar energy.

Herein, the $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ membrane was prepared through sol–gel-hydrothermal method supported on glass substrates. Lastly, the Pt as the co-catalyst was deposited on the surface of membrane and the $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane was obtained and used as a visible-light photocatalyst for the photocatalytic hydrogen evolution with simultaneous photocatalytic degradation of pollutants (glycerol, phenol and Na_2S/Na_2SO_3) under visible-light irradiation. Meanwhile, some main influence factors on the visible-light photocatalytic hydrogen evolution activity of $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane were investigated. Furthermore, the mechanism of up-conversion luminescence process of $Er^{3+}:Y_3Al_5O_{12}$ and the visible-light photocatalytic hydrogen evolution principle of $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane under visible-light irradiation were also proposed.

2. Experimental

2.1. Materials and apparatus

Er_2O_3 (99.999 % purity), Y_2O_3 (99.999 % purity) and $Al(NO_3)_3 \cdot 9H_2O$ (analytically pure), citric acid (analytically pure) and HNO_3 (65–68 %, analytically pure) (Veking Company, China) were used to synthesize the $Er^{3+}:Y_3Al_5O_{12}$ as up-conversion luminescence agent. Tetrabutyl titanate (TBT) ($Ti(OBu)_4$, $C_{16}H_{36}O_4Ti$, analytically pure, Sinopharm Chemical Reagent Co., Ltd., China) as titanium dioxide (TiO_2) precursor was used to prepare the TiO_2 membrane. Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 97 % purity, Sinopharm Chemical Regent Co., Ltd, China) was used as co-catalyst precursor for preparing the $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ photocatalysts. Glycerol ($C_3H_8O_3$, analytically pure), phenol (C_6H_5OH, analytically pure) and Na_2S/Na_2SO_3 (analytically pure, Veking Company, China) were used as model pollutants to examine the visible-light photocatalytic hydrogen evolution activity of $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrance. All the reagents were of analytical purity grade, and were used without further purification. Experiments were conducted in a photocatalytic reactor. The volume of the reactor was 500 mL. The outside of the reactor was a water-jacketed to keep a stable reaction temperature (25 °C). The sheet glass (75 mm (length) × 25 mm (width) × 2.2 mm (thickness)) was used as the supports of $Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane. 300 W xenon lamp (LX-300, 400–800 nm wavelength range, Deruifeng hardware electrical appliance businesses, China) was used as simulated visible-light irradiation source.

2.2. Preparation of visible-light photocatalyst ($Er^{3+}:Y_3Al_5O_{12}/Pt–TiO_2$ membrane)

2.2.1. Synthesis of $Er^{3+}:Y_3Al_5O_{12}$ as up-conversion luminescence agent

The synthesis of $Er^{3+}:Y_3Al_5O_{12}$ as up-conversion luminescence agent by the sol–gel and calcination method was carried out with the following procedure. Er_2O_3 (0.0128 g) and Y_2O_3 (2.2715 g) powders were dissolved in HNO_3 aqueous solution (30 mL, 50%) with magnetic stirring and heated (about 60 °C) until transparent to obtain $Y(NO_3)_3$ and $Er(NO_3)_3$ solutions. $Al(NO_3)_3 \cdot 9H_2O$ (12.6208 g) was dissolved into 150 mL deionized water. All the aluminum nitrate solution was added to the above transparent solution and the homogenous solution was obtained. Then, citric acid as chelating agent and co-solvent was added into the above mixture solution (mol ratio of citric acid: metal ion is 3:1). The remaining solution was stirred and heated at 50–60 °C until the transparent sol was successfully prepared. Then, the sol was heated at 80 °C for 24 h and the xerogel was finally obtained, which was ground into fine homogeneous powders. The powders were heated at 500 °C for 50 min, and then continue to heat to 1100 °C and kept for 2.0 h and allowed