



Solvothermal fabrication of La-WO₃/SrTiO₃ heterojunction with high photocatalytic performance under visible light irradiation

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ABSTRACT

A series La-doped WO₃/SrTiO₃ heterojunctions photocatalyst were successfully prepared using solvothermal method. The as-fabricated heterostructures composite included La-doped WO₃ fluff spheres tightly grew on the surface of SrTiO₃ cubic particles. The crystallinity, structural, morphological and optical features of the catalysts were characterized using several techniques including XRD, XPS, SEM, TEM UV – vis and HRTEM. The photocatalytic activity of the heterojunction was evaluated by the photocatalytic degradation of methyl orange (MO) under visible-light irradiation. The influence of La doping and SrTiO₃ molar ratio on heterojunctions photocatalysts was investigated. Among the as-prepared photocatalysts, the LWS50 sample exhibited the highest photocatalytic activity, almost 100% MO were completely decomposed within 75 min under visible light irradiation ($\lambda > 420$ nm). Compared with the pure WO₃ and SrTiO₃, the enhancement of photocatalytic activity was mainly attributed to the three-dimensional hierarchical structure and the effectively transfer and separation of photogenerated electron–hole pairs in La doped WO₃ and SrTiO₃ heterojunctions

1. Introduction

In the modern society, on account of the rising threats of global energy crisis and environment issues, semiconductor photocatalysts has attracted increasing attention owing to its utilization of pollution-free, clean, renewable and abundant natural sun light as a source of energy [1–4]. Among the semiconductor photocatalysts, perovskite strontium titanate (SrTiO₃) has been widely studied as one of the few promising materials due to its excellent photocatalytic activity, chemical stability, and interesting structure compatibility. SrTiO₃ can split water under UV irradiation without external bias because their conduction band levels are 200 mV more negative than the redox potential for H₂ evolution. However, the low quantum efficiency hindered its practical application due to the rapid recombination of photo-generated charges and theoretical maximum of solar energy utilization caused by the wide bandgap (3.2 eV) [5,6]. Namely, SrTiO₃ can only utilize ultraviolet light, which occupies less than 4% of the whole solar spectrum, thus leading to low photocatalytic activity. Therefore, it is crucial for increasing the solar energy utilization and limiting the fast charge recombination through the modification of SrTiO₃, including the adjusting band gap semiconductors by doping or co-doping semiconductors with cations

[7–9] and forming heterojunction structures by coupling two or more different catalysts [10,11]. Among these methods, the construction of a heterojunction structure is a very efficient route to eliminate these drawbacks. In recent years, SrTiO₃ coupling with oxide materials have been widely reported, such as SrTiO₃/TiO₂ [12] SrTiO₃/g-C₃N₄ [13], SrTiO₃/ZnO [14], SrTiO₃/Ag₃PO₄ [15] and SrTiO₃/CeO₂ [16], etc.

Compared to the above mentioned oxide, tungsten trioxide (WO₃) has caught the sight of the researchers as photocatalysts, because of its high photocatalytic activity, environmentally benign nature, non-toxicity and inexpensive, etc. WO₃ can harvest the visible lights well to enhance the photocatalytic activities, due to its narrow bandgap energy ranges from 2.6 to 3.0 eV. Furthermore, WO₃ has more positive valence band edge than the famous benchmark photocatalyst TiO₂, provided a sufficient driving force to evolve oxygen to oxidize organic compounds in contaminated water under visible light irradiation [17–21]. Even though WO₃ has these promising characteristics, the efficiency of the pure WO₃ is still confined by the fast recombination of photo-generated charge carriers. Therefore, it is still necessary to further improve its efficiency as a photocatalyst. Recently, rare earth element doped photocatalysts semiconductor nanoparticles have received much attention due to its dominant advantage, for example, larger atomic radii and

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electron-rich outer shell [22–27]. It was reported that the band structure, grain size, BET surface, optical structure and the photocatalytic activity of the resultant solid solutions could be greatly influenced by the rare earth ions doping due to their different outer shell electrons. Especially, under the light irradiation, the rare earth ions doped in the photocatalyst crystal lattice works as electron scavenger, which can trap the superoxide species and thus effectively inhibit the hole–electron recombination. For example, Lan et al. [28] reported that La ions doping could efficiently suppress the phase transformation from high active anatase into the less active rutile phase and recombination efficiency of electron–hole pairs. Meksi et al. [29] reported that La-doping could increase the amount of oxygen vacancies on the TiO₂ surface due to the charge imbalance. Moreover, incorporation of lanthanide ions into TiO₂ matrix could hinder the crystal growth, reduce the size of particles, increase the surface area, and promote the strong adsorption of the reactants on the photocatalyst surfaces. All these above factors also contribute to the improvement of photocatalytic activity.

Recently, erbium–nitrogen co-doped SrTiO₃ have been fabricated in our group by a facile solvothermal method and shown much better photoactivity than that of pure SrTiO₃, due to its larger surface area, more surface active sites and stronger absorption bands in the visible light region in comparison with that of pure SrTiO₃ and TiO₂ (P25). However, up to date, there were very few reports on introduction of lanthanum ions into the structure of WO₃ and their photocatalytic activities towards the degradation of methyl orange (MO) solution under visible light irradiation. In order to further improve the photocatalytic activity of photocatalytic materials, La doped WO₃/SrTiO₃ heterojunction composites were rationally designed by a facile and reproducible way in this paper. The photocatalytic performances of the La-WO₃/SrTiO₃, single La-WO₃ and SrTiO₃ were contrastively evaluated by examining the degradation of MO to simulate the industrial wastewater under visible-light irradiation. Interestingly, La-WO₃/SrTiO₃ photocatalysts required shorter irradiation time for complete mineralization MO than pure La-WO₃ and SrTiO₃. Furthermore, the influence of different molar ratio between WO₃ and SrTiO₃ on the photocatalytic activity of La-WO₃/SrTiO₃ nanocomposites was also discussed in this work.

2. Experimental section

2.1. Materials

All chemicals were of analytical pure reagent and purchased commercially without further purification. Titanium dioxide (TiO₂), strontium carbonate (SrCO₃), concentrated sulfuric acid (H₂SO₄ 98 wt% aqueous solution), ethanol (C₂H₆O) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Sodium tungstate dehydrate (Na₂WO₄·2H₂O), citric acid monohydrate (C₆H₈O₇·H₂O), lanthanum nitrate (La(NO₃)₃·6H₂O) were purchased from Aladdin Chemical Reagent Co. Ltd. Distilled water was used throughout the whole experiment.

2.2. Sample preparation

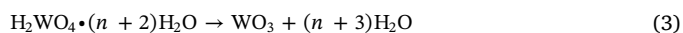
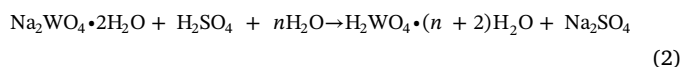
SrTiO₃ particles were prepared by a conventional solid state reaction. A mixture of stoichiometric quantities of SrCO₃ and TiO₂ was ground for 1 h. After that, the mixture was put in a platinum pot, and then calcined in air at 1100 °C for 2 h, as shown in Eq. (1).



The product was washed with distilled water and then dried at 60 °C overnight to obtain pure SrTiO₃ particles compound to reserve.

La doped WO₃ nanocomposites were obtained as follows: 0.0115 mol of Na₂WO₄·2H₂O was dissolved in 50 mL of water under violently stirring. Then, 5 mL of concentrated H₂SO₄ was added into the

above solution drop by drop with vigorous stirring. Precipitation was immediately formed with white color, and gradually changed to light yellow, as follow the Eqs. (2) and (3).



After that, the yellow precipitation was separated from the reaction solution by centrifugation, washed with water two times and dried in a vacuum at 60 °C overnight. Then, the particles were dissolved in 75 mL 1.1 M citric acid aqueous solution. Subsequently, 0.0038 mol of lanthanum nitrate was added into the aqueous solution to prepare the precursor solution at a nominal atomic ration of La : W = 0.3 : 1.

Finally, the La ion doped WO₃/SrTiO₃ nanocomposites was carried out by a solvothermal reaction. Then, varied amounts of as-prepared SrTiO₃ was added into the above precursor solution to ensure that the nominal atomic Sr/W ratio was 25%, 50%, 75%, 100%, respectively. (For brevity, the above as-prepared samples were labeled as LWS25, LWS50, LWS75, LWS100, respectively.) After continuous stirring for two days, the mixture solution was transferred into a Teflon-lined stainless steel autoclave up to 80% of the total volume, followed by solvothermal heated at 180 °C for 24 h. After the reaction, the obtained precipitate was washed with water and ethanol for three times, and finally dried in a vacuum at 60 °C for 12 h. In addition, La doped WO₃ (La-WO₃) without adding SrTiO₃ was also prepared under the same reaction conditions.

2.3. Characterization

The phase purity and crystal nature of samples was determined by powder X-ray diffraction (XRD, Bruker AXS, D8-Advance) using monochromatized Cu-Kα radiation (λ = 1.54 Å). The morphologies and nanostructure of samples were observed by a field-emission scanning electron microscope (FE-SEM, Hitachi SU8000) and transmission electron microscopy (TEM, JEM-2100) High-resolution TEM (HRTEM) was obtained by Tecnai F30 FEI with accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by on a surface area and pore size analyzer (Quantachrome Instruments, Autosorb-iQ) using nitrogen as absorbent at 77 K. The surface composition and elemental status of the specimens were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo). The optical properties were performed for the samples using a Lambda 950 UV/Vis-NIR spectrophotometer, in which barium sulfate (BaSO₄) was used as the standard with 100% reflectance.

2.4. Photocatalytic activity measurement

Photochemical reaction was carried out in a Pyrex reactor with a capacity of 500 mL using a 300 W Xenon lamp (CHF-XM500) as light source with a UV light (420 nm) cut-off filter. The inner cell had thermostated water flowing through a jacket between the mercury lamp and reaction chamber and it was constructed of Pyrex glass, which cut the UV emission of the mercury below 290 nm. Prior to the reaction, the solution was deaerated by bubbling with N₂ (20 kPa) for 30 min to remove O₂ and CO₂ dissolving in water. The photocatalytic activity of the samples was inspected by the photocatalytic degradation of methyl orange (MO). In a typical experiment, 0.1 g catalyst was dipped in 100 mL methyl orange solution with an initial concentration of 5 mg/L. The pH of the solution was adjusted to 2 using 1 mL/L HCl. Prior to light irradiation, the solution was magnetically stirred in the dark for half h to establish adsorption-desorption equilibrium between the organic molecules and the catalyst surface. Moreover, the degradation of MO was also carried out without catalyst to deduct light irradiation effect. Afterward, the lamp was turned on, and 4 mL suspension was taken out every 15 min and was centrifuged to separate the

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