Materials Science in Semiconductor Processing 89 (2019) 201–211

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Heterojunction formation on $InVO_4$/N-TiO_2 with enhanced visible light photocatalytic activity for reduction of 4-NP

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ARTICLE INFO

Keywords:
Photocatalysis
$InVO_4$/N-TIO_2
Heterojunction
4-NP photoreduction

ABSTRACT

In this study, we report the preparation of a new heterojunction photocatalyst of $InVO_4$/N-TiO_2 (labeled as TNI) by a simple coupled process using sol gel method. Compared to the weak response with pure N-TiO_2, and $InVO_4$, the new hybrid materials were found to significantly enhance photoreduction of 4- Nitrophenol (4-NP) to 4-Aminophenol (4-AP) under visible light. The increase in photocatalytic activity was attributed to several factors such as the development of a synergistic effect between N-Doped TiO_2 and $InVO_4$ materials allowing a greater absorption of light in the visible region of the solar spectrum and to the formation of heterojunctions in the TNI materials which improve the separation of photogenerated electron-hole pairs and decreases the recombination process. Based on the characterization results and the photoactivity experiments we propose a general scheme describing the 4-NP photocatalytic reduction mechanism using the TNI composites. Finally the great stability of the heterostructures was evaluated by means of photocatalysts recycling tests.

1. Introduction

Titanium dioxide (TiO_2) is one of the most used photocatalysts due to its important properties such as great oxidative potential, chemically stable, economical, abundant and non-toxic material [1]. However, TiO_2 only absorbs UV light at wavelengths below 388 nm, which represents only about 4% of the solar spectrum, while 43% of solar spectrum is in the visible range [2]. Therefore, the development of efficient photocatalysts particularly sensitive to visible light is necessary for a more efficient use of solar energy in photocatalysis. TiO_2 doping with non-metals is considered one of the best and most promising techniques to extend its response to visible light [3], additionally; non-metal doping is a low cost effective method in comparison to noble metal doping. TiO_2 has been doped with numerous elements such as N, C, or S [4]. Among them, nitrogen has been widely used because it can generate overlapping orbital between the 2p orbital of N with the O2p orbital of the TiO_2 valence band [5], which is reflected in a decrease of the band gap of TiO_2, furthermore induces a decrease in the recombination rate of the photogenerated pairs (e^-/h^+) and better photocatalytic performance under visible light. Although it has been reported that N-doped TiO_2 show enhanced photocatalytic performance, its efficiency is too low for utilizing the most visible range of the solar spectrum, which would greatly hinder the large scale use such a technology [6]. Recent research has shown that the combination of two or more semiconductors with appropriate energy levels to produce a suitable composite structure may be a good strategy to overcome previous deficiencies [7,8].

In this way, to increase the photo-efficiency, several studies have been recently focused on the production of new materials with improved response to visible light based on binary heterojunctions (HJs) of TiO_2 and narrow band gap semiconductors (E_g) such as TiO_2-WO_3 [9], TiO_2-CdS [10], TiO_2-Bi_2WO_6 [11], TiO_2-BiOI [12], TiO_2-In_2O_3 [13], TiO_2-Ag_2O [14] TiO_2-Cu_2O [14]. These HJs showed enhancement photocatalytic activity due to strong interfacial interaction between TiO_2 and the semiconductor interface, which eventually promotes the generation of more and highly reactive oxygen species (ROS) i.e., superoxide anion radical ($^{\bullet}O_2^-$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($^{\bullet}OH$) leading to a higher photocatalytic performance of HJs for the degradation of pollutants [15].

On the other hand, among the various photoactive materials, indium vanadate ($InVO_4$) has attracted considerable attention since it has proved to be an excellent photocatalyst in the visible light region. Due to its superior semiconductor properties, it can directly divide water and carried out the photodegradation of organic contaminants [16,17]. $InVO_4$ has a relatively narrow band range (2.02–2.10 eV) and is therefore photoactive under visible light irradiation [18]. In stark contrast, the pure $InVO_4$ exhibits minimal photocatalytic activity due to its very low specific surface area ($S_{BET} < 5\ m^2g^{-1}$) that limit its

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https://doi.org/10.1016/j.mssp.2018.09.017
Received 6 March 2018; Received in revised form 15 September 2018; Accepted 19 September 2018
Available online 26 September 2018
1369-8001/

adsorption capacity as well as fast recombination of charge carriers.

$InVO_4$ coupled with others semiconductors have been recently reported for enhancement photocatalytic activity and to overcome the fast recombination of charge carriers. For example, Feng et al. [19] fabricated $BiVO_4/InVO_4$ composite photocatalysts by a facile hydrothermal method. Thus achieving an increased visible light driven catalytic activity towards the degradation of rhodamine B. Meng et al. [20] synthesized Z-scheme $InVO_4$/CdS HJs photocatalysts by microwave-assisted, followed by a mild hydrothermal method. All HJs exhibited excellent activity in the degradation of rhodamine B and ciprofloxacin under visible light irradiation. Using a hydrothermal process, Hu et al. [21] synthesized g-C_3N_4/ $InVO_4$ heterojunctions photocatalyts in situ growth of $InVO_4$ nanoparticles onto the surface of g-C_3N_4. An effective separation of charge carriers and stronger reducing power caused enhanced H_2 evolution from water splitting compared with bare g-C_3N_4 and $InVO_4$ composites. MoS_2-$InVO_4$ heterostructures were synthesized as efficient photocatalysts for photocatalytic H_2 production. The positive effect of intimate nanojunctions formed between MoS_2 and $InVO_4$ resulted in the excellent visible-light-responsive [22]

Several studies has shown that the addition of $InVO_4$ to TiO_2 produces a red shift in the absorption edge for the composite [23,24]. This indicates that the $InVO_4/TiO_2$ composite materials may be active in visible-light-induced photocatalysis.

Shen et al. [25] fabricated 3D hierarchical porous $TiO_2/InVO_4$ nanocomposites by loading TiO_2 nanoparticles on the surface of porous $InVO_4$ microspheres. $TiO_2/InVO_4$ nanocomposites showed increasing photodegradation rate than the corresponding pure $InVO_4$ sample. $InVO_4/TiO_2$ nanojunction composites were synthesized by an ion impregnate method, the nanocomposites shown an improved absorption in the visible light region and excellent performance in the methyl orange photodegradation [26]. Xiao et al. [27] prepared $InVO_4/TiO_2$ mesoporous photocatalyst by a sol-gel method with enhancement visible-light driven photocatalytic activity in the degradation of volatile organic compounds (VOCs). Zhao et al. [28] synthesized $InVO_4/TiO_2$ nanocomposites via sol-gel process. The photocatalytic activity of the composites increased for more than 2 folds by incorporating small amount of $InVO_4$ into TiO_2 under sunlight irradiation.

Compared with bare TiO_2, an N-doped TiO_2 offers a large surface area and visible light absorption. The fabrication of a heterojunction with $InVO_4$ allowed a closed contact with to form a material with enhanced absorption in the visible range. Moreover the $InVO_4$ particles could effectively replace the use of rare, expensive noble metals, like Pt, as a cocatalyst and thus leads to a highly desirable, cost-effective and environmentally friendly. To the best of our knowledge, there is no report regarding N-TiO_2 and $InVO_4$ binary HJs as an efficient visible light activated photocatalyst.

In this study, we report a new simple method for the preparation of a series of composites of TiO_2 doped with nitrogen (N-TiO_2) and $InVO_4$ with the aim of extending the light absorption spectrum toward the visible region. The $InVO_4$ samples were synthesized by the hydrothermal method. The N-$TiO_2/InVO_4$ composite were prepared by the sol gel method. The photocatalytic performance of all samples was studied in detail by investigating the photocatalytic reduction of 4-NP to 4-AP under visible light illumination ($\lambda > 420$ nm). 4-AP is an important added value compound since it is used in the fabrication of a great number of fine chemicals [29,30]. The improved photocatalytic performance of these new materials based on binary HJs together with a probable mechanism has been investigated and discussed in detail. To the best of our knowledge, this is the first report showing the preparation of $InVO_4$/N-TiO_2 photocatalytic HJs via the sol gel method and this use in photoreduction of 4-NP to 4-AP under visible light irradiation. This work may provide new insights into the preparation of novel highly photoactive $InVO_4$/N-TiO_2 materials under visible light irradiation.

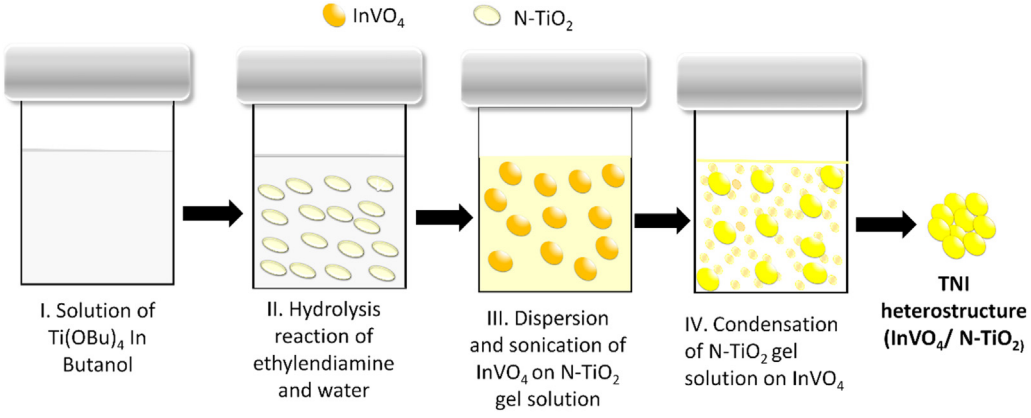
2. Materials and methods

2.1. Synthesis of orthorhombic $InVO_4$

The synthesis of $InVO_4$ was carried out as follows: Indium nitrate ($In(NO_3)_3{\cdot}xH_2O$) was dissolved in nitric acid (HNO_3) and the solution was named A; ammonium metavanadate (NH_4VO_3) was dissolved in ammonia (NH_4OH) and the solution was named B. Solution B was slowly added in A at a molar ratio of 1:1, then, the resulting solution was kept under continuous stirring for 2 h to keep the reagents mixed uniformly. Afterwards, the pH of the solution was adjusted to about 7 with 2 M ammonia solution. The obtained sol was then placed in a stainless steel autoclave; the temperature of the hydrothermal reaction was 200 °C for 6 h. The material obtained was centrifuged and washed with deionized water 3–5 times, and finally the sample was dried at 60 °C for 6 h using a heating rate of 1 °C/min.

2.2. Synthesis of the $InVO_4$/N-TiO_2 photocatalyst

The series of $InVO_4$/N-TiO_2 heterostructures materials were synthesized by the sol gel method by the hydrolysis of titanium butoxide Ti$(OBu)_4$ at room temperature and by varying the amounts of $InVO_4$ as shown in Scheme 1. In a typical sol gel synthesis, titanium butoxide (8 mL) was dissolved in 40 mL of butanol. The mixture was magnetically stirred for about 2 h. Ethylenediamine was added as the hydrolysis catalyst (N:Ti molar ratio 2:1) and nitrogen doping source to the sol solution and stirred during 4 h. Afterwards, the solution was hydrolyzed by adding 15 mL of a mixture of ethanol-water (1:1). Then, the stirring is increased until the gel is broken and stabilized. Later, the as-prepared $InVO_4$ is added and the mixture was sonicated for 90 min and this suspension was kept under continuous stirring for 48 h. The xerogel was



Scheme 1. Formation of TNI heterostructures by the sol gel method.