Highly Efficient Solar Hydrogen Evolution by Photoelectro-Chemical Water Splitting over ZnFe$_2$O$_4$-ZnO Heterojunction

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Abstract. ZnFe$_2$O$_4$-ZnO heterojunction thin-films were fabricated by the composite photocatalyst, which was first synthesized by a freeze-drying process and followed by a simple chemical bath way in the condition of low temperature. The ZnFe$_2$O$_4$-ZnO heterojunction thin-film exhibited high efficiency to get hydrogen with photoelectrochemical method under visible-light irradiation. The property with photoinduced charge-transfer of p-type ZnFe$_2$O$_4$ was improved significantly by Cooperating with n-type ZnO. The heterojunction at the interface between the ZnO and ZnFe$_2$O$_4$ efficiently reduced the recombination of photoinduced electron-hole pairs, and thus increasing the lifetime of charge carriers and enhancing the photo-to-current efficiency of the ZnFe$_2$O$_4$-ZnO heterojunctions. It was found the heterostructure between two different kinds of semiconductors is important in affecting the dynamic properties of the photo-to-current conversion efficiency and their photogenerated charge carriers.

1. Introduction

Hydrogen has many advantages and is expected to be the excellent energy material in human future, but its production is mostly coming from fossil fuels at the present time [1]. Alternatively, photocatalytic and photoelectron-chemical water-splitting for hydrogen production provides a promising method for environmentally friendly, low-cost, and clean production of H$_2$ by solar energy. Honda and Fujishima’s early work has reported the TiO$_2$ photoelectrochemical hydrogen production. [2] Subsequently, technical and scientific interests have grown significantly in semiconductor photocatalysis. Then, several different semiconducting catalytic materials have been reported as catalyst for photoelectron-chemical to get hydrogen Products [3-4]. The wide band-gap semiconductor ZnO has been considered as an important material widely found in electronic, sensor, photovoltaic, optical, and spintronics applications [5]. On the other hands, it has been found that many spinel type or perovskite- complex oxides have photoactivity of visible-light-driven. Among them, spinel ZnFe$_2$O$_4$ which has a relatively narrow bandgap (1.9 eV), attracts much attention in the application of solar energy [6-7].

ZnFe$_2$O$_4$ can be deposited on the surface of n-type semiconductors, such as TiO$_2$, SrTiO$_3$, Fe$_2$O$_3$, to fabricate a composite photoelectrode in order to further improve the photocatalytic activities [8]. Hou et al. observed an enhanced photoelectrochemical performance by depositing ZnFe$_2$O$_4$ nanoparticles on the surface of TiO$_2$ nanotube arrays using electrochemical deposition process [9]. Hence, ZnFe$_2$O$_4$-ZnO provides an ideal choice to integrate all the different properties together in a single nanostructure.
with superior functionality [10]. However, the fabrication of ZnFe$_2$O$_4$-ZnO heterojunction with tunable functionality and well-defined morphology still remains challenging.

In this paper, ZnO was first synthesized by a novel freeze-drying method, the obtained materials have a hierarchical structure, which is beneficial to the formation of more ZnFe$_2$O$_4$ heterostructures in the following step. The ZnFe$_2$O$_4$-ZnO nanocomposite thin-film photoelectrode was fabricated from the powder suspension solution onto fluorine-doped tin oxide (FTO) glass by dip-coating. The photoelectrochemical hydrogen production performance of ZnFe$_2$O$_4$-ZnO and ZnO NRA nanocomposite photoelectrodes were investigated and compared. Highly efficient solar hydrogen evolution by photoelectrochemical water splitting over the ZnFe$_2$O$_4$-ZnO heterojunction was established.

2. Experimental Section

2.1. Materials
All chemicals containing Fe(NO$_3$)$_3$•9H$_2$O, Zn(CH$_3$COO)$_2$•2H$_2$O, NH$_3$•H$_2$O, C$_2$H$_5$O, are analytical purity and used in the present experiments.

2.2. Synthesis of ZnFe$_2$O$_4$
The as-prepared ZnFe$_2$O$_4$ was synthesized by a freeze-drying method synthesis. Typically, dissolve 3.0 g of Zn (CH$_3$COO)$_2$•2H$_2$O in 100 mL water. When it dissolved completely, Add 3.5 mL of ammonia into the above solution. Then, stirred for 15 min. Later, Put the beaker with the obtained transparent solution in a water bath at 80 ℃ for 40 minutes and cooled naturally to room temperature. After that, we can get the white powder by centrifugation. Ethanol solution was used to wash the white powder several times, and then freeze-dried at -60℃ to obtain a pure phase ZnO material. Fe (NO$_3$)$_3$•9H$_2$O was dissolved in deionized water to prepare 1.0 mM, 2.0 mM, 3.0 mM, 4.0 mM, 5.0 mM, 6.0 mM Fe(NO$_3$)$_3$•9H$_2$O solutions. 100.0 mg of the prepared ZnO was added to 25 ml of Fe (NO$_3$)$_3$•9H$_2$O solutions of different concentrations and stirred for 20 minutes. Water should be used to wash the obtained powder several times, and then dried at 60℃ for 12 h.

2.3. Characterization of the Products
We used a Bruker D8 X-ray diffractometer with Cu Kα radiation to record X-ray powder diffraction (XRD) patterns. The measurement range of 2θ was from 10° to 80°. The surface morphologies of the catalysts were seen by a SEM (JSM-6700F). Diffuse reflection spectroscopy was performed using a Beijing Universal Analysis T9 UV-Vis spectrometer (UV-vis), which can detect a maximum range of 200–800nm. Shimadzu RF-5301PC fluorescence spectrophotometer was used to measure the photoluminescence (PL) spectrum.

2.4. Photoelectrochemical Measurements
The photoelectrochemical test uses the currently recognized three-electrode system, that is, the produced material is used as the working electrode, reference electrode is the silver/silver chloride electrode, and the platinum sheet electrolyte is applied as the counter electrode. The simulated sunlight source is PLS-SXE300 xenon lamp. In the experiment, the electrochemical workstation was a CompactState.H10800 electrochemical workstation from the Netherlands. First cut the FTO glass into 1.5 × 1 cm$^2$, clean it with detergent, and then ultrasonically clean it in alcohol for 60 minutes. Take 40 mg of the ground photocatalyst and pour it into 40 mL of acetone. After 15 minutes of ultrasonic shock, electrophoresis was set at 10 V for 5 minutes. The electrophoresis electrode was FTO glass. After that, the prepared electrode sheet was put into a tube furnace, and the temperature was raised to 200 ℃ at a temperature increase rate of 2 ℃/min, followed by baking for 2 hours.
3. Results and Discussions

3.1. The Crystal Structure
The XRD patterns of the pure ZnO and zinc ferrate-ZnO composite materials with various amounts of Fe ions are shown in figure 1. It can be seen from the XRD patterns that all diffraction peaks of the product can be indexed to the pure cubic phase of ZnO. This observation indicated that the novel freeze-drying method can be used to synthesize pure-phased ZnO sample. Moreover, with the addition of Fe$^{3+}$ in the synthesis process, the single-phase ZnFe$_2$O$_4$ (JCPDS NO. 22-1012) can be synthesized using the above mentioned solvothermal crystallization process.

![Figure 1. X-ray diffraction patterns of the synthesized ZnFe$_2$O$_4$-ZnO heterojunction.](image)

3.2. The Morphologies of ZnO and ZnFe$_2$O$_4$-ZnO Heterojunction
Figure 2 shows the scanning electron microscopic (SEM) images of the ZnO and ZnFe$_2$O$_4$-ZnO composite heterojunction. As it can be seen from figure 2a, there are many vacant sites on the surface of ZnO, which are formed by freeze-drying process. After the ice crystals formed in the freezing process was evaporated, there will be formed the vacancy. When ZnO is crystallized, the vacancy is retained, thus forming a hierarchical porous structure. Figures 2b and 2c showed the morphologies of the ZnFe$_2$O$_4$-ZnO composite heterojunction. The morphology of the ZnO changed significantly after the ZnFe$_2$O$_4$ nanoparticles formed. The ZnO surface was composed with a large amount of nanoparticle materials.

![Figure 2. Scanning electron microscopic images of the ZnO and ZnFe$_2$O$_4$-ZnO composite heterojunctions: (a) ZnO; (b) ZnFe$_2$O$_4$-ZnO ([Fe$^{3+}$]=2 mM/L); (c) ZnFe$_2$O$_4$-ZnO ([Fe$^{3+}$]=4 mM/L).](image)

3.3. The Photophysical Property
Figure 3 shows the UV-Vis diffuse reflectance spectra of the ZnO and ZnFe$_2$O$_4$-ZnO composite materials. The band gap of ZnO is 3.1 eV, which is consistent with the wavelength absorption range of ZnO. After loading ZnFe$_2$O$_4$, the absorption range is extended to about 700 nm, which is close to the...
1.86 eV band gap of ZnFe$_2$O$_4$. However, the absorption intensity of the ZnFe$_2$O$_4$-ZnO composite photoelectrode in the ultraviolet region is higher, indicating that a p-n heterojunction is established at the interface between ZnO and ZnFe$_2$O$_4$, and an electric field is formed. This electric field reduces the recombination of photo-generated electrons and holes, so the absorption intensity of the ZnFe$_2$O$_4$-ZnO composite photoelectrode in the ultraviolet region is increased.

**Figure 3.** UV-Vis diffuse reflection spectra of ZnO and ZnFe$_2$O$_4$/ZnO composite photocatalyst.

3.4. The Raman Spectra of ZnO and ZnFe$_2$O$_4$-ZnO Heterojunction

Raman scattering measurements demonstrated that ZnFe$_2$O$_4$ structure has been formed. Figure 4b presents the Raman spectra of ZnO and ZnFe$_2$O$_4$-ZnO composite photoelectrode. For the spectra of ZnO, the vibration at 436 cm$^{-1}$ can be classified as Zn-O [11]. The spectra of the ZnFe$_2$O$_4$-ZnO composite materials in the range of 50-800 cm$^{-1}$ were fitted with four thick lines at 355, 437, 640, and 684 cm$^{-1}$. Modes above 600 cm$^{-1}$ are generally considered to be of the A$_{ig}$ type and involve the movement of O in the tetrahedral AO$_4$ group. Therefore, two vibrations above 600 cm$^{-1}$ may be due to the simultaneous existence of two AO$_4$ groups, and A is iron or zinc. The other low frequency modes is the characteristics of the octahedral sites (BO$_6$). The Fe-O vibration of ZnFe$_2$O$_4$ is located in the band at 355 cm$^{-1}$ and the band at 640-684 cm$^{-1}$ [12]. Therefore, the Raman spectra means that ZnFe$_2$O$_4$ is a spinel structure. Moreover, the broad bands in the range of 640 cm$^{-1}$ and 684 cm$^{-1}$ indicate that ZnFe$_2$O$_4$ is in the form of very small particles on the bulk ZnO. [13] The quantum size effect caused by ZnFe$_2$O$_4$ nanoparticles, leads to the broadening of the Raman peak.

**Figure 4.** Raman spectra of ZnO and ZnFe$_2$O$_4$/ZnO composite photoelectrode.
3.5. The Photoluminescence Spectra of ZnO and ZnO-ZnO Heterojunction

Photoluminescence (PL) emission has been developed as a sensitive technique for semiconductor analysis and the emission mainly originates from direct reorganisation of the photogenerated carrier in semiconductor. The lower the PL spectral intensity, the more difficult it is for photo-generated carriers to recombine. PL spectra were used to study the charge recombination and transfer efficiency of ZnO nanorods and ZnO-ZnFe$_2$O$_4$ composites. Figure 5 shows the PL spectra of ZnO and ZnFe$_2$O$_4$-ZnO nanocomposites. It can be found that the spectral intensity of pure ZnO is higher, which is attributed to the severe reorganisation of photo-generated carriers. However, because of the introduction of ZnFe$_2$O$_4$, the fluorescence was quenched significantly for ZnFe$_2$O$_4$-ZnO coupling system (figure 5), which means that the separation of photogenerated carriers is enhanced. The higher electron-hole separation rate of the ZnFe$_2$O$_4$-ZnO coupled system due to the two reasons: (1) The separation rate of the photogenerated carrier in the coupled system is higher than that of a single ZnO. (2) ZnFe$_2$O$_4$ and ZnO form a Type II heterostructure, and a space charge region will be formed at the interface of the heterojunction. This charge region can greatly affect its photoelectrochemistry performance.

![Figure 5. Photoluminescence emission spectra of ZnO and ZnFe$_2$O$_4$-ZnO composite photoelectrode.](image)

3.6. The Photo-to-Current Property

The photoelectrochemical performances of pure phase ZnO and ZnFe$_2$O$_4$-ZnO composite photoelectrodes were investigated in a three-electrode photoelectrochemical cell under visible light. The working electrodes of the ZnO and ZnFe$_2$O$_4$-ZnO films were fabricated by the electrophoretic deposition. From figure 6, both ZnFe$_2$O$_4$-ZnO photoelectrodes showed much higher photocurrent density than the pure phase ZnO photoelectrode. From photocurrent density, the hydrogen production performances of ZnO and ZnFe$_2$O$_4$-ZnO composite photoelectrodes can be investigated.

The ZnFe$_2$O$_4$-ZnO photoelectrode synthesized from 4 mM/L Fe$^{3+}$ generates a photocurrent density of 6.0 $\mu$A·cm$^{-2}$, which is 6 times as much as a single ZnO photoelectrode. Clearly, the Photoelectrochemical performance of ZnFe$_2$O$_4$-ZnO composite photoelectrode has been greatly enhanced. As such, the composite material will help inhibit the recombination of the charge, and enhancements in the photo-to-current conversion efficiency would be achieved. Two reasons may result in the promotion of the photoelectrochemical hydrogen production performance. One is that ZnFe$_2$O$_4$ is a visible light responsive film. Another is the p-n junction heterojunction electric field, which is formed on the junction between ZnO NRA and ZnFe$_2$O$_4$, it can effectively separate the photo-generated carriers. It is accepted that the Fermi level of ZnFe$_2$O$_4$ is much closer to the valence band potential than to the conduction band potential. When ZnFe$_2$O$_4$ was composited with ZnO, the Fermi level potential of the composite photoelectrode will be positively pulled to ZnFe$_2$O$_4$. At the same time, the flat band potential will shift to a positive potential, thus resulting in the positive shift of the onset potential of photo-induced current. Meanwhile, the photogenerated current density of ZnFe$_2$O$_4$-ZnO composite photoelectrode increased greatly compared to ZnO photoelectrode.
4. Conclusions

We have succeeded in loading amorphous ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles onto the ZnO surface using a simple freeze-drying method. The photoelectrochemical hydrogen production performance of ZnFe\textsubscript{2}O\textsubscript{4}-ZnO composite photoelectrode is significantly improved. It depends on the constitution of p-n junction electrical field on the boundary surface between ZnFe\textsubscript{2}O\textsubscript{4} and ZnO, as well as the visible light absorption ability of ZnFe\textsubscript{2}O\textsubscript{4}. ZnFe\textsubscript{2}O\textsubscript{4} sensitized ZnO composite photoelectrode exhibits good stability in the photocatalytic water splitting to produce hydrogen. Therefore, ZnFe\textsubscript{2}O\textsubscript{4}-ZnO composites have good potential for photocatalytic water splitting.

Reference
[1] Tong H, Ouyang S, Bi Y, Umezawa N, Oshikiri M, Ye J 2012 Nano-photocatalytic Materials: Possibilities and Challenges Adv. Mater. 2012 (24) 229-251
[2] Kudo A, Miseki Y 2009 Heterogeneous photocatalyst materials for water splitting Chem. Soc. Rev. 2009 (38) 253-278
[3] Anchieta C G, Cancelier A, Mazutti M A, Jahn S L, Kuhn R C, Gündel A, Chiavone-Filho O, Foletto E L 2014 Effects of solvent diols on the synthesis of ZnFe\textsubscript{2}O\textsubscript{4} particles and their use as heterogeneous photo-Fenton catalysts Materials 7 (9) 6281-6290
[4] T. Welderfael, O. Yadav, A.M. Taddesse, J. Kaushal. 2013 Synthesis, characterization and photocatalytic activities of Ag-N-codoped ZnO nanoparticles for degradation of methyl red Chem. Soc. Ethiop 221-232
[5] Moreira E, Fraga L, Mendonça M, Monteiro O 2012 Synthesis, optical, and photocatalytic properties of a new visible-light-active ZnFe\textsubscript{2}O\textsubscript{4}-TiO\textsubscript{2} nanocomposite material Nanopart. Res. 1-10
[6] Fan G, Tong J, Li F 2014 Visible-Light-Induced Photocatalyst Based on Cobalt-Dope Zinc Ferrite Nanocrystals Journal of Alloys and Compounds 602 228-234
[7] Lei Zou, Haoran Wang, Guoliang Yuan, Xiong Wang. 2018 Magnetically Separable CdS/ZnFe\textsubscript{2}O\textsubscript{4} Composites with Highly Efficient Photocatalytic Activity and Photostability under Visible Light ACS Appl. Nano Mater. 2018 (1) 831-838
[8] Yongsheng Guo, Ningsi Zhang, Xin Wang, Qinfeng Qian, Shiyi Zhang, Zhaosheng Li Zhigang Zou. 2016 A facile spray pyrolysis method to prepare Ti-doped ZnFe\textsubscript{2}O\textsubscript{4} for boosting photoelectrochemical water splitting J. Mater. Chem. A 2017 (5) 7571–7577
[9] Liu J, Zhao Y, Shi L, Yuan S, Fang J, Wang Z, Zhang M 2011 Solvothermal Synthesis of Crystalline Phase and Shape Controlled Sn\textsuperscript{4+}-Doped TiO\textsubscript{2} Nanocrystals: Effects of Reaction Solvent ACS Appl. Mater. Interfaces 2011 (3) 1261-1268
[10] Hou G, Zhang Y, Gao S. 2017 Enhanced visible-light photocatalytic activities of flower-like ZnFe\textsubscript{2}O\textsubscript{4}, decorated with Ag\textsubscript{2}PO\textsubscript{4} nanoparticles Materials Letters. 209
[11] Hongjin Lv, Liang Ma, Peng Zeng, Dingning Ke, Tianyou Peng. 2010 Synthesis of floriated
ZnFe$_2$O$_4$ with porous nanorod structures and its photocatalytic hydrogen production under visible light. *Journal of Materials Chemistry* **20** (18) 3665-3672

[12] Li X, Hou Y, Zhao Q 2011 A general, one-step and template-free synthesis of sphere-like zinc ferrite nanostructures with enhanced photocatalytic activity for dye degradation *Journal of Colloid & Interface Science* **358** (1) 102

[13] Xing Z, Ju Z, Yang J, Xu H, Qian Y 2012 One-step hydrothermal synthesis of ZnFe$_2$O$_4$, nano-octahedrons as a high capacity anode material for Li-ion batteries *Nano Research* **5** (7) 477-485