Photoelectrochemical Properties of Nanomultiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ *pn* Junction Photoelectrodes

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Supporting Information

ABSTRACT: Nanomultiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ *pn* junctions are prepared by a pulsed laser deposition method to explore their photoelectrochemical properties as the photoelectrodes. It is demonstrated that the multiple-*pn*-junction structure is favorable to enhancing the photocurrent density and the onset potential of the photoelectrode. Furthermore, the 20-junction photoelectrode-based PEC cell yields a high open circuit photovoltage of up to 0.97 V, which is much higher than that for a single *pn* junction photoelectrode PEC cell that yields an open circuit photovoltage of 0.13 V. A multiple-junction band structure model is assumed to describe the behavior of the CaFe$_2$O$_4$/ZnFe$_2$O$_4$ multiple-junction photoelectrodes. It is suggested that the open circuit photovoltage is dominated by the number of *pn* junctions in a multiple-junction photoelectrode and the carrier transfer inside the photoelectrode is improved by narrowing the single-layer thickness. These findings provide a new approach to designing the multiple-junction structure to improve the PEC properties of the photoelectrodes.

INTRODUCTION

Since Fujishima and Honda discovered water photolysis on the TiO$_2$ photoelectrode, hydrogen production through a photoelectrochemical (PEC) approach has emerged as one of the most promising technologies because it represents an easy way to convert solar energy into chemical energy.\(^1\) In a PEC cell, the photoelectrode is the most important part; it harvests incident light, generates electron–hole pairs, and performs PEC reactions on the surface.\(^2,3\) Over the past decades, significant progress has been made in the development of photoelectrodes with various configurations and materials.\(^4-26\) Among them, the multilayer photoelectrodes have attracted a lot of attention, owing to the advantages of enhancing the light utilization,\(^25,24\) or providing a photovoltage to assist PEC water splitting.\(^25,26\) In multilayer photoelectrodes, a semiconductor *pn* junction usually functions as a photovoltaic cell to provide a photovoltage.\(^25,26\) Another advantage of separating the electron and hole resulting from the depletion region of *pn* junction has attracted little attention. In the case of a single-layer semiconductor photoelectrode, the depletion region, which efficiently separates the electron and hole, exists only in a small region (tens of nanometers) at the electrode–electrolyte interface.\(^25\) Most of the area inside the photoelectrode belongs to the neutral region, which does not possess the ability to separate the electron and hole. By fabricating nanomultiple *pn* junction photoelectrodes, numerous depletion regions could be created even inside the photoelectrode. It is worth expecting that the nanomultiple *pn* junction structure could enhance the electron–hole separation and the carrier transfer, thus resulting in the improvement of the PEC properties.

However, there are two issues that need to be addressed pertaining to the multiple-junction thin film being utilized as a photoelectrode. (1) Does the carrier transfer driven by the *pn* junctions favor the PEC performance of the *pn* junction photoelectrodes? As the photoelectrode, the *p* semiconductor acts as a cathode for the PEC reduction reaction (*p*-cathode) and the *n* semiconductor acts as an anode for PEC oxidation reaction (*n*-anode) because of the effect of the depletion region at the electrode–electrolyte interface.\(^1,4\) Nevertheless, a conventional *pn* junction could drive only the photogenerated electron transfer from the *p* side to the *n* side under light irradiation (*n*-cathode).\(^28\) This electron transfer does not favor the application of *pn* junction as the photoelectrode. (2) Can the carrier transfer continuously in multiple-junction thin films? In the multiple-junction thin films, there are two kinds of space charge fields with opposite electronic field directions existing. An important question is whether the carrier can be transferred through these opposite space charge fields. It should be noticed

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that, as the photoelectrodes, the multiple-junction photoelectrodes are immersed in the electrolyte and an additional depletion region exists at the electrode-electrolyte interface. This unique depletion region at the electrode-electrolyte interface is supposed to greatly change the performance of the multiple-junction thin films as a photoelectrode.

Here, we reported the fabrication of nanomultiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ pn junction photoelectrodes by a pulsed laser deposition (PLD) method. The PEC properties of the multiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ pn junction photoelectrodes were discussed in detail. It was found that the multiple-junction structure could significantly promote the PEC properties of the photoelectrodes, including the photocurrent density and the onset potential. On the basis of the experiment evidence, a multiple-junction band structure model was assumed to describe all of the behavior of the multiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ pn junction photoelectrodes.

**EXPERIMENTAL SECTION**

The thin films were prepared by the pulsed laser deposition (PLD) method using CaFe$_2$O$_4$ and ZnFe$_2$O$_4$ pellets as the targets and fluorine-doped tin oxide (FTO) as the substrate. The targets and FTO glass were set on the PLD machine (ST-PLD; Pascal Co., Japan), and the distance between the targets and FTO glass was set to be 5 cm. After that, the film-preparation chamber of the PLD machine was evacuated to 0.001 Pa, and then pure O$_2$ was introduced into the chamber until the pressure became 4 Pa. After the FTO glass was heated to 550 °C, the target was irradiated with a Nd:YAG laser at a wavelength of 355 nm. The repetition rate and the energy of the laser pulse length were 10 Hz and 62 mJ per pulse, respectively. After PLD deposition, the temperature was maintained for 1 h in the presence of O$_2$ ($9.6 \times 10^4$ Pa) for postheat treatment of the samples.

The multilayer p-CaFe$_2$O$_4$/n-ZnFe$_2$O$_4$ junction electrodes with a single-layer thickness of 10–15 nm were prepared via the following steps: (I) depositing a ZnFe$_2$O$_4$ layer for 2.5 min and (II) depositing a CaFe$_2$O$_4$ layer on a prepared ZnFe$_2$O$_4$ layer for another 2.5 min. The processes (I and II) were repeated many times (10, 15, 20, and 25).

A field-emission scanning electron microscope (JSM-6701F, JEOL) and a transmission electron microscope (TEM, JEOL Co.) were used to characterize the samples. The cross-sectional TEM sample was prepared by Ga$^+$ focused ion beam (FIB) milling performed on a JEOL-9310 machine with a lift-out technique. The sample was milled to a thickness of less than 50 nm to make sure of the beam permeation. The microstructure was observed with a JEOL 300 keV electron microscope.
field-emission TEM (JEM-3000F) and a JEOL Cs-corrected dedicated scanning TEM (JEM-2500FES) equipped with a Gatan 766 EELS spectrometer (Enfina 1000).

PEC properties of as-prepared thin films were characterized with an electrochemical station (ALS/CH model 650A) using three-electrode and two-electrode configurations. Platinum and Ag/AgCl were used as the counter electrode and reference electrode, respectively. In the photoelectrochemical measurement, the as-prepared electrodes were illuminated by light from the side of the electrolyte/film interface in aqueous Na2SO4 solution (0.1 M) through a quartz window. A 500 W xenon lamp (Optical Module X, USHIO, Japan) was utilized as the light source.

**RESULTS AND DISCUSSION**

$p$-CaFe2O4/n-ZnFe2O4 were adopted to explore the PEC properties of the multiple-junction thin films. CaFe2O4 and ZnFe2O4, which possess a favorable chemical stability in the aqueous solution, are naturally formed p-type and n-type oxide semiconductors, respectively. n-ZnFe2O4 provides a much more negative Fermi level (0.3 V versus Normal Hydrogen Electrode (NHE)) in comparison to $p$-CaFe2O4 (1.0 V vs NHE). Therefore, it is reasonable to fabricate the pn heterojunction using CaFe2O4 and ZnFe2O4. Furthermore, the photoelectrodes for PEC water splitting, CaFe2O4 and ZnFe2O4 possess identical narrow band gaps of 1.9 eV, which result in abundant visible light harvesting.

In addition, the conduction band edge of CaFe2O4 is located at −0.6 V versus NHE and the valence band edge of ZnFe2O4 is at +2.0 V versus NHE. It is feasible to use a CaFe2O4/ZnFe2O4 pn junction for splitting water (H2 reduction at 0 V vs NHE and O2 oxidation at 1.23 V vs NHE).

The PLD method was utilized to prepare the multiple CaFe2O4/ZnFe2O4 pn-junction thin films. By changing the laser irradiation targets (CaFe2O4 and ZnFe2O4 pellets) back and forth, the CaFe2O4/ZnFe2O4 multilayer was prepared simply on a fluorine-doped tin oxide (FTO) substrate. Meanwhile, by controlling the laser irradiation time on a target, the thickness of each layer was adjusted accurately. Here, it should be noticed that all the CaFe2O4/ZnFe2O4 multiple-junction thin films [FTO/(ZnFe2O4/CaFe2O4)] were composed by the direct tandem connection of the CaFe2O4/ZnFe2O4 junctions. Figure 1a presents the transmission electron microscope (TEM) image of a 15-junction photoelectrode [FTO/(ZnFe2O4/CaFe2O4)15] with a single-layer thickness of about 10−15 nm. The bright-field TEM image of cross-section viewing (Figure 1a) displays the layer structure clearly because of the notable contrast resulting from the composition difference between neighboring CaFe2O4 and ZnFe2O4 layers. The compositions of multiple layers are further investigated by using electron energy loss spectroscopy (EELS) analysis (Figure 1b,c). The EELS spectra confirm the composition of both CaFe2O4 and ZnFe2O4 layers. Moreover, elemental maps (Figure 1d,e) indicate that the Fe and O elements spread evenly throughout all layers but Zn and Ca are distributed only in respective layers with apparent boundaries. These results provide solid evidence for the CaFe2O4/ZnFe2O4 multilayer structure.

The PEC properties of this 15-junction photoelectrode [FTO/(ZnFe2O4/CaFe2O4)15] are measured in a 0.1 M Na2SO4 aqueous solution using a three-electrode configuration with Pt and Ag/AgCl electrodes as the counter electrode and reference electrode, respectively. In the current density versus potential ($J$-$V$) graph, a photocathodic current density is observed (red line, Figure 2) when the applied potential is more negative than 0.98 V versus Ag/AgCl. This result indicates that the 15-junction photoelectrode acts as the cathode for the PEC reduction reaction. Compared to the single-layer CaFe2O4 photocathode (the same thickness with this 15-junction photoelectrode), the 15-junction photoelectrode exhibits a much larger photocurrent density (−16.87 μA/cm2 at 0.2 V vs Ag/AgCl) and a much more positive onset potential (0.98 V vs Ag/AgCl). These results show that the multiple-junction thin film has a significant enhancement effect on the PEC properties, including the photocurrent density and the onset potential. These results also imply that the multiple-junction structure should be favorable for improving the performance of the photoelectrode.

To clarify the mechanism of the multiple-junction photoelectrodes throughout, we start from studying the PEC properties of the thin films, which are the basic compositions of the CaFe2O4/ZnFe2O4 multiple junction (such as single-layer CaFe2O4, single-layer ZnFe2O4, and single CaFe2O4/ZnFe2O4 pn junction thin films). All of these samples were fabricated by the PLD method on FTO substrates. The compositions of as-prepared CaFe2O4 and ZnFe2O4 single-layer thin films were successfully confirmed by using Raman spectroscopy as shown in Figure 3a,b.22,23 Because these single-layer thin films and the multiple-junction thin films were prepared under the same experimental conditions (the same target, pressure, laser power, and substrate temperature), these Raman spectra also could be considered to be indirect evidence of CaFe2O4 and ZnFe2O4 compositions in the multiple junctions. Figure 4a shows $J$-$V$ curves of the CaFe2O4 and ZnFe2O4 photoelectrodes. Typical photocathode and photoanode properties are observed on these two single-layer photoelectrodes, respectively. A photocathodic current, which should be due to the PEC reduction reaction, is observed on single-layer $p$-CaFe2O4 thin films, and a photoanodic current, which should be due to the PEC oxidation reaction, is observed on a single-layer $n$-ZnFe2O4 thin film. For a single-layer semiconductor electrode, whether the semiconductor acts as a photocathode or a photoanode is determined by the depletion region at the electrode–electrolyte interface (called the electrode DR). For example, in the $p$-type semiconductor electrode, the electrode DR fulfills the function of driving the electron to the surface of the photoelectrode. Thus, the $p$-type electrode is suitable as a cathode for the photoelectrode. Another characteristic of the photocathode is a positive open circuit photovoltage ($V_{oc}$), which also results from the...
electron−hole separation caused by the electrode DR. As the inset of Figure 4c shows, under 118 μW/cm² of 430 nm monochromatic light, a single-layer CaFe₂O₄ electrode exhibits a positive V_{oc} of about 0.04 V (measured using the three-electrode configuration).

In comparison to these two single-layer electrodes, the pn junction (FTO/ZnFe₂O₄/CaFe₂O₄) photoelectrode shows a negative photocurrent and a positive photovoltage V_{oc}' (0.025 V under 430 nm monochromatic light, 118 μW/cm²), which means that the CaFe₂O₄/ZnFe₂O₄ pn junction electrode acts as cathode with a p-CaFe₂O₄ layer as the surface contacting the electrolyte (Figure 4b,c). Different from the single-layer electrode, in the pn junction electrode there is another depletion region of the pn junction (called the junction DR), influencing the electron−hole transfer inside the photoelectrode. Therefore, the measured open circuit photovoltage V_{oc}' of the pn junction electrode should be equal to V_{oc} + V_{jn}.\(^{33}\) Here, V_{oc} is the photovoltage generated by the electrode DR, and V_{jn} is the photovoltage generated by the junction DR. The CaFe₂O₄/ZnFe₂O₄ pn junction PEC cell presents positive

Figure 3. Raman spectra of the single-layer CaFe₂O₄ and ZnFe₂O₄ thin films.

Figure 4. (a) J−V graph of a single CaFe₂O₄ electrode, with the inset showing a J−V graph of a single ZnFe₂O₄ electrode. (b) J−V graph of a CaFe₂O₄/ZnFe₂O₄ pn junction electrode. (c) V−t graph of a CaFe₂O₄/ZnFe₂O₄ pn junction electrode at 0.1 V vs Ag/AgCl, with the inset showing a V−t graph of a single CaFe₂O₄ electrode at 0.1 V vs Ag/AgCl (430 nm monochromatic light source, 118 μW/cm²; measured using a three-electrode configuration).
Based on the results above, we clarify the function of single seconds of light-on, also re (Figure 4c) shows that the photovoltage and further narrow the depletion region of circuit photovoltage (could di pn Thus photovoltage (Vpn) of the pn junction electrode presents a positive open circuit photovoltage (Voc = Voc + Vpn < 0) (Figure 5a). After

\[ V_{oc}'(+) \] which is consistent with \( V_{oc}(+) \) but opposite to \( V_{pn}(-) \). This implies that the electrode DR took predominance over the junction DR in the PEC performance of the pn junction electrode. The potential–time (V–t) graph (Figure 4c) shows that the photovoltage fluctuated in the initial seconds of light-on, also reflecting the competition between \( V_{oc} \) and \( V_{pn} \). It is suggested that the built-in of \( V_{oc} \) is slower than that of \( V_{pn} \) after light-on (The electrode–solution system need more time to reach steady state after light irradiation in comparison to pn junction). At the beginning of light irradiation, the incomplete built-in \( V_{oc}(+) \) is smaller than \( I \) \( V_{pn}(-) \), so pn junction electrode presents a negative open circuit photovoltage \( (V_{oc} = V_{oc} + V_{pn} > 0) \) (Figure 5b).

![Figure 5. (a) Band structure of CaFe\(_2\)O\(_4\)/ZnFe\(_2\)O\(_4\) junction at the sudden of the light irradiation. (b) Band structure of CaFe\(_2\)O\(_4\)/ZnFe\(_2\)O\(_4\) junction under the light irradiation after getting stable.](image)

V\(_{oc}\) is built-in completely, \( |V_{oc}(+)\) becomes larger than \( |V_{pn}(-)| \). Thus pn junction electrode presents a positive open circuit photovoltage \( (V_{oc} = V_{oc} + V_{pn} > 0) \) (Figure 5b). The open circuit photovoltage results also reflect the important effect of electrode DR in the performance of the pn junction photoelectrode. In conventional light-irradiated pn junction, electron only could travel from p-layer to n-layer under the force of \( V_{pn} \). However, in pn junction photoelectrode PEC cell, \( V_{oc}(+) \) generated by electrode DR applies across the pn junction as the bias. This large \( V_{oc}(+) \) could neutralize \( V_{pn}(-) \) and further narrow the depletion region of pn junction. Thus, with the assistance of \( V_{oc}(+) \), the electron in n-ZnFe\(_2\)O\(_4\) layer could diffuse to p-CaFe\(_2\)O\(_4\) layer across the narrowed depletion region of pn junction. Thus, a negative photocurrent is generated in pn junction photoelectrode based PEC cell. Based on the results above, we clarify the function of single CaFe\(_2\)O\(_4\)/ZnFe\(_2\)O\(_4\) pn junction photoelectrodes in a PEC cell. It is suggested that the performance of pn junction electrode should be determined by electrode DR and junction DR jointly. While the effect of electrode DR is stronger than junction DR, the pn junction with p-layer as the surface acts as photocathode (such as this CaFe\(_2\)O\(_4\)/ZnFe\(_2\)O\(_4\) pn junction photoelectrode). Oppositely, while the effect of junction DR is stronger than electrode DR, the pn junction photoelectrode with p-layer as the surface acts as the photoanode.

After understanding the performance of single pn junction photoelectrodes, we further studied the effect of the pn junction number on the PEC properties of the multiple-junction photoelectrodes. Four multiple-junction photoelectrodes with the same single-layer thickness of 10−15 nm but different pn junction numbers (10, 15, 20, and 25) were prepared by PLD method. The PEC properties of these four samples are showed in Figure 6c. With the increase of pn junction number from 10 to 20, the photocurrent density and the onset potential are improved remarkably. The 20-junction photoelectrode shows the highest photocurrent density (−25.23 μA/cm\(^2\) at 0.2 V vs Ag/AgCl) and the most positive onset potential (1.10 V vs Ag/AgCl) in all four samples. Furthermore, the open circuit photovoltages of all four samples were measured with a two-electrode configuration. As Figure 6b shows, the open circuit photovoltage \( (V_{oc}) \) shows the same changing trend with the photocurrent result. \( V_{oc} \) increases significantly with the increase of the junction number and reaches the highest value of 0.97 V on the 20-junction photoelectrode. Figure 6a shows the \( V−t \) curves of the 20-junction photoelectrode and the single pn junction photoelectrode with the same total thickness. With the light on, the PEC cell of 20-layer CaFe\(_2\)O\(_4\)/ZnFe\(_2\)O\(_4\) photoelectrode yielded a \( V_{oc} \) of 0.97 V; it was about 5 times higher than that of a single-layer junction photoelectrode (0.13 V). The enhancement of the photovoltage is suggested to be due to the increased pn junction number in the multiple-junction photoelectrodes but not to the thickened semiconductor layer thickness because the thickening of the layer thickness is reported to influence only the value of the photocurrent density but not the open circuit photovoltage and the onset potential. It is suggested that the enhanced photovoltage generated by the multiple-junction photocathodes results in the improvement of the PEC properties. With the contribution of the self-generated photovoltage, the photocathodic current appears at a more positive potential; meanwhile, the photocurrent density is improved significantly. It is a novel result that the multiple-junction photoelectrode could generate a large open circuit photovoltage, the value of which is determined by the pn junction number in the multiple-junction photoelectrode. This result exhibits a new potential approach to providing a photovoltage for improving the PEC properties, besides using a specialized photovoltaic cell that need a tunnel layer to connect with the PEC semiconductor layer.

We also studied the effect of the single-layer thickness on the PEC properties of the multiple-junction photoelectrodes. Three samples with the same total thickness but different layer thicknesses were fabricated by the PLD method: a 10-junction photocathode with a single-layer thickness of about 10−15 nm (12.5 nm on average) [FTO/(12.5 nm ZnFe\(_2\)O\(_4\)/12.5 nm CaFe\(_2\)O\(_4\))]\(_{10}\), a 5-junction photocathode with a single-layer thickness of about 25 nm [FTO/(25 nm ZnFe\(_2\)O\(_4)/25 nm CaFe\(_2\)O\(_4\))]\(_{5}\), and a single pn junction with single-layer thickness of about 125 nm [FTO/125 nm ZnFe\(_2\)O\(_4)/125 nm CaFe\(_2\)O\(_4\)].
The $J$–$V$ curves of these three samples are shown in Figure 7. The 5-junction and 10-junction photoelectrodes show much higher photocurrent densities than a single $pn$ junction photoelectrode. The photocurrent density of the 10-junction photoelectrode is higher than that of the 5-junction photoelectrode in the region from 0.33 to 0.80 V versus Ag/AgCl but lower than that of the 5-junction photoelectrode in the region from −0.20 to 0.33 V versus Ag/AgCl. Compared to a single $pn$ junction photoelectrode, the multiple-junction samples with different single-layer thicknesses both show the obvious enhancement effect on the PEC properties. Furthermore, the multiple-junction photoelectrode with a 12.5 nm single-layer thickness could efficiently enhance the photocurrent density at the relative positive potential (0.33 to 0.80 V vs Ag/AgCl). In contrast, the multiple-junction photoelectrode with a 25 nm single-layer thickness could efficiently enhance the photocurrent density in the relatively negative potential region (−0.20 to 0.33 V vs Ag/AgCl). These results indicated that the single-layer thickness greatly influences the PEC properties of the multiple-junction photoelectrodes. The multiple-junction photoelectrode with thin single-layer thickness shows an obvious negative photocurrent at a relative positive potential, reflecting the fact that the multiple-junction structure with a thin single-layer thickness is helpful in reducing the dependence of PEC properties on the applied potential.

On the basis of the experimental results above, we assumed a model to depict the function of the multiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ $pn$ junction photoelectrodes. Figure 8c presents the assumed schematic diagram of the multilayer CaFe$_2$O$_4$/ZnFe$_2$O$_4$ $pn$ junction photoelectrode, which is treated as a series of interconnected $pnp$ junctions. The calculated thickness of the electrode DR at the CaFe$_2$O$_4$-layer-electrolyte interface was about 2.8 nm (calculation process in the Supporting Information). Therefore, it is rational that the electrode DR is located only in the outmost CaFe$_2$O$_4$ layer and fulfills its function of separating an electron and a hole completely even when the single-layer thickness was decreased to the 10 nm scale. Because the thickness of single layer is only 10−15 nm,
the neutral region is quite small and the depletion region fill most of the region of the multiple pn junction. First, we focus on the outermost pn-junction, of which p₁ contacts the electrolyte. For a conventional pnp junction under light irradiation without contacting the electrolyte, symmetrical space charge fields $E_{p_1,p_2}$ and $E_{n_1,n_2}$ should generate two photovoltages with the same amplitude in opposite directions ($V_{p_2,n_1} = -V_{n_1,p_2}$), as shown in Figure 8a. Thus, the total photovoltage ($V_{pnp}$) of pnp junction should be zero. While the pnp junction is set as the electrode, the electrode DR generates an additional positive photovoltage as the bias on the pnp junction (Figure 8b). The positive photovoltage ($V_{oc}$) was in agreement with $E_{n_1,p_2}$ but in conflicting with $E_{p_1,p_2}$. Thus, $E_{p_1,p_2}$ was strengthened while $E_{n_1,p_2}$ was weakened. As a result, $E_{n_1,p_2}$ yielded a positive photovoltage ($V_{p_2,n_1}$) with a larger amplitude than that of the negative photovoltage ($V_{n_1,p_2}$) yielded by $E_{n_1,p_2}$. This indicates that $V_{pnp} = V_{p_2,n_1} + V_{n_1,p_2} > 0$ and that the total photovoltage ($V_{p_2,n_1,p_2}$-solution) of the p₂₁n₁₁p₂-dollar system is greater than $V_{oc}$ because of $V_{p_2,n_1,p_2}$-solution $= V_{p_2,n_1} + V_{oc} > V_{oc}$.

As to the next p₂₁n₂₁p₂ junction on which a positive $V_{p_2,n_1,p_2}$-solution is applied, similar reasoning leads to such a conclusion that $V_{p_2,n_1,n_2,p_2}$-solution $> V_{p_2,n_1,p_2}$-solution. Accordingly, the rest may be deduced by analogy. If we assume that $N$ is the layer number, then $V_{p_1,n_2,p_2}$-solution $> V_{p_2,n_1,p_2}$-solution. This model could explain the phenomenon that the open circuit photovoltage increases gradually with the increase in the pn junction number in a photoelectrode. However, it should be noticed that the photovoltage generated by each pnp junction is greatly influenced by the intensity of absorbed light. The increase in the pn junction number indicates that the inner pnp junctions could absorb very little light and could not supply the resulting photovoltage. In the competition between the multiple-junction enhancement effect and the limitation of light absorption, the 20-layer CaFe₂O₄/ZnFe₂O₄ heterojunction has the best PEC properties.

Another important issue is the transfer of a photogenerated carrier in the multiple CaFe₂O₄/ZnFe₂O₄ pnp junction. As illustrated in Figure 8c, under the force of the photovoltaic $V_{oc}$ and the applied potential, the holes transfer from p₁ to n₁ through the narrowed p₁-n₁ depletion region. Then, the holes diffuse across the neutral region of n₁ within their lifetime because the single-layer thickness was as small as around several dozen nanometers. After the depletion region between n₁ and p₂ is entered, under the force of the enlarged space charge field the holes move to the interface of n₁ and p₂ where the holes recombine completely with the electrons from p₂. By parity of reasoning, the following pnp junctions repeated analogous carrier transportation. This assumed carrier transfer route could explain the effects of the different single-layer thicknesses on the PEC properties. The depletion region of a pn junction usually has a fixed thickness depending on the materials in the pn junction, so the increase in the single-layer thickness directly enlarges the area of the neutral region. In the sample with a thick single-layer thickness, the neutral region is still large so that most of the carriers do not easily diffuse across the neutral region of the n layer in their lifetime. Enhancing the applied potential (in the negative direction) could widen the depletion region between n₁ and p₂ and thus narrow the neutral region, so the photocurrent density increases drastically from 0 as the applied potential becomes negative gradually. For the sample with a thin single-layer thickness, the neutral region of the junction is thinner so that most of the carriers could transfer through the neutral region even at a relative positive applied potential, so the multiple-junction photoelectrode with thin single-layer thickness exhibits an obvious photocurrent at a
relative positive applied potential. However, it should be noticed that the photocurrent density of the multiple-junction photoelectrode should be determined by the photocurrent density generated by the single pnp junction because the carrier of a single pnp junction could recombine only with the carrier from the neighboring pnp junction. The photocurrent density of a single pnp junction is strongly determined by the intensity of absorbed light, which is directly influenced by the single-layer thickness. With this limitation, the photocurrent density of the multiple-junction photoelectrode with a thin single-layer thickness did not show a remarkable improvement when the applied potential became much more negative.

From the results above, it is clarified that the multiple-junction structure is favorable for improving the PEC properties of the photoelectrodes. The increase in the junction number in a multiple-junction photoelectrode enhances the open circuit photovoltage remarkably. The nanomultiple-junction structure in the photoelectrode favors the carrier transfer and reduces the dependence of PEC properties on the applied voltage. With the joint effect of these two advantages, the multiple-junction photoelectrode exhibits wonderful PEC properties (a high photocurrent density and a favorable onset potential). Our results provide a potential approach to reducing the dependence of the PEC properties on the applied potential. It should be helpful in improving the efficiency of PEC water splitting further.

**CONCLUSIONS**

Multiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ p–n junction thin films were prepared successfully by the PLD method. These multiple-junction photoelectrodes had an obvious enhancement effect on the PEC properties, including the photocurrent density and the onset potential. The multiple CaFe$_2$O$_4$/ZnFe$_2$O$_4$ p–njunction photoelectrodes also yielded a high open circuit photovoltage up to 0.97 V. It is found that the multiple-junction structure could enhance the open circuit photovoltage efficiently and improve the carrier transfer inside the photoelectrodes. Our results provide a novel approach to reducing the dependence of PEC properties on the applied potential and also raising the possibility of utilizing the multiple-junction structure to improve the PEC properties of the photoelectrodes.

With regard to the decrease of the effective and improve the carrier transfer inside the photoelectrodes. Our results provide a novel approach to reducing the dependence of PEC properties on the applied potential and also raising the possibility of utilizing the multiple-junction structure to improve the PEC properties of the photoelectrodes.

**ASSOCIATED CONTENT**

4 Supporting Information

Information for the p-CaFe$_2$O$_4$/n-ZnFe$_2$O$_4$ photoelectrode. This material is available free of charge via the Internet at http://pubs.acs.org.

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