Fabrication of a TiO2/Fe2O3 Core/Shell Nanostructure by Pulse Laser Deposition toward Stable and Visible Light Photoelectrochemical Water Splitting

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ABSTRACT: Here, we report the fabrication of TiO2/Fe2O3 core/shell heterojunction nanorod arrays by a pulsed laser deposition (PLD) process and their further use as photoelectrodes toward high-performance visible light photoelectrochemical (PEC) water splitting. The morphology, phase, and carrier conduction mechanism of plain TiO2 and TiO2/Fe2O3 core/shell nanostructure were systematically investigated. PEC measurements show that the TiO2/Fe2O3 core/shell nanostructure enhances photocurrent density by nearly 2 times than the plain ones, increases visible light absorption from 400 to 550 nm, raises the on/off separation rate, and delivers high stability with only a 3% decrease of current density for tests of even more than 14 days. This work provides a method to design an efficient nanostructure by combination of a facile hydrothermal process and high-quality PLD process to fabricate a clean surface and excellent crystallinity for charge separation, transfer, and collection toward enhanced PEC properties.

1. INTRODUCTION

Photoelectrochemical (PEC) water splitting is one of the promising methods to directly convert solar energy to chemical energy by using semiconductor electrodes. Since the discovery of Fujishima and Honda in 1972, various photo-materials have been fabricated for PEC water splitting systems toward high stability and efficiency. Compared with other well-known wide gap metal oxides like ZnO, SnO2, and SrTiO3, TiO2 exhibits several prominent properties such as chemical stability, high charge mobility, and low cost. Li et al. reported a new TiO2 structure with a nanofiber template to have a quite high current density. Liu et al. made a black TiO2 with the use of Ar and Ar/H2 gas to achieve more light absorbance for a higher hydrogen production rate. Wu et al. demonstrated a Bi-TiO2 nanostructure to deliver high performance. Obviously, it is still very challenging to accomplish an excellent efficiency by TiO2 alone as its light absorption ability is limited by the wide band gap only for UV light, which is a small part of the full spectrum. In consideration of expanding light absorption ability, hematite (α-Fe2O3) is one of the most promising candidate materials due to its narrow band gap (~2.0 eV), good response to visible light, environmental friendliness, earth abundance, and the conduction band edge position for possible water splitting at a low voltage. Yu et al. prepared a quite high-performance hematite photoanode by the pulsed laser deposition (PLD) approach and further used more FeOOH loading on the hematite layer to have nearly 0.8 mA cm−2 at 1.23 V versus reversible hydrogen electrode (RHE). Wang et al. demonstrated a Sn-doped hematite nanoflake to increase the photocurrent. Han et al. reported a Sb-doped SnO2 (ATO) with Fe2O3 nanorods for water splitting, and the efficiency of the best sample has increased 139% higher than that of the pure hematite nanorods at 1.23 V RHE. However, it is noticed that their devices demand complicated experiment processes and additional added materials, which would restrict inevitably the practical applications in the future.
Even up to now, it is still difficult to succeed a high-performance electrode by only one material due to the great restriction of the individual’s own flaws. Photogenerated charges require efficient separation followed by fast transportation to inject into the respective reduction and oxidation reactions, but the charges are very tough to be generated and separated in one material alone. We argue that we could expect to build a core/shell nanostructure, in which a high charge mobility material as a core improves the transmission efficiency of photoinduced charges and a wide light spectrum absorption material as a shell enhances the visible light response and charges separation.20−22 Yang et al. prepared a TiO2/BaTiO3 core/shell nanostructure, which produced a high photocurrent, but both materials could absorb only UV light.23 Wang et al. devised Fe2O3/TiO2 core/shell photoelectrodes to improve separate efficiency of photoinduced charge carriers and absorb visible light.24 Smith et al. reported TiO2/WO3 and WO3/TiO2 core/shell nanorod arrays to combine optical utilization and water splitting efficiency together.25 Though these works used various types of materials, they chose the same facile way to prepare the nanostructure by using arrays as a core and high-quality materials as a shell. PLD is a powerful tool for depositing thin films with great precision in thickness and quality at a controllable laser intensity and frequency.26−29 The high-quality target and feathering deposition process of PLD endorse the perfect ability to produce conformal ultrahigh-quality films under a low temperature.

Figure 1 shows the SEM image of the morphology of TiO2 nanorod arrays and the sample after Fe2O3 loading. Figure 1a shows uniform and typical TiO2 nanorod arrays with about 150 nm diameter and a smooth top-side. From Figure 1b, we can see that the length of TiO2 nanorods is about 1.8 μm, which has been viewed as the suitable thickness for charge transport.24,30 Also, different lengths of TiO2 have been prepared, which could be found in Figure S1, and the 1.8 μm sample shows the best performance. Figure 1c,d gives the representative top-view and

2. RESULTS AND DISCUSSION
Figure 1 shows the SEM image of the morphology of TiO2 nanorod arrays and the sample after Fe2O3 loading. Figure 1a shows uniform and typical TiO2 nanorod arrays with about 150 nm diameter and a smooth top-side. From Figure 1b, we can see that the length of TiO2 nanorods is about 1.8 μm, which has been viewed as the suitable thickness for charge transport.24,30 Also, different lengths of TiO2 have been prepared, which could be found in Figure S1, and the 1.8 μm sample shows the best performance. Figure 1c,d gives the representative top-view and
cross-sectional SEM images of TiO$_2$/7 min Fe$_2$O$_3$ core/shell nanostructures, which were measured as the best samples in the following discussion. During the PLD process, high energy laser pulses bombard the surface of the Fe$_2$O$_3$ target and deposit it onto TiO$_2$. From the top-view SEM image of Figure 1c, there is only little roughness change on the surface and all nanorods have similar morphologies. From the cross-sectional image of Figure 1d, we can identify that the top-side and down-side have nearly the same surface. We also prepared a 30 min long deposited time sample from which we can see that the morphology has been totally changed with a large amount of Fe$_2$O$_3$ (Figure S2). Through the comparison before and after the deposition of Fe$_2$O$_3$, we can see that a uniform film is well prepared by using PLD technology.

To discuss the crystallization state and the uniformity of the nanostructure after PLD Fe$_2$O$_3$ deposition, the XRD pattern (Figure 2a) was used here.

![Figure 2](image)

**Figure 2.** (a) XRD patterns of FTO glass and TiO$_2$/7 min Fe$_2$O$_3$ core/shell nanostructure. (b) HRTEM of the TiO$_2$/7 min Fe$_2$O$_3$ core/shell nanostructure.

However, the characteristic peaks of Fe$_2$O$_3$ are hard to detect owing to the short depositing time, but the peaks of TiO$_2$ can be detected easily due to its excellent crystallinity, which can be indexed to the rutile type (JCPDS no. 88-1175). To further identify Fe$_2$O$_3$, we deposited Fe$_2$O$_3$ on Si under the same experimental condition, and the XRD pattern could be found in Figure S3 from which we can see the peak of Fe$_2$O$_3$. From the HRTEM image (Figure 2b), we can see more details about the sample of the TiO$_2$/7 min Fe$_2$O$_3$ nanostructure. The image shows that the Fe$_2$O$_3$ thin film has a high-quality crystalline structure with a clean external surface and ~9 nm thickness, which is good for charge transport. The selected area electron diffraction (SAED) pattern (Figure S4) of TiO$_2$/7 min Fe$_2$O$_3$ shows that it has very high crystallinity. A larger scale of Fe$_2$O$_3$ could be found in Figure S5 from which the surface of Fe$_2$O$_3$ is still clear. The TEM and SAED images of the TiO$_2$ sample in Figure S6 show that the TiO$_2$ nanorod has the (110) plane. In addition, it would be pertinent to mention that the surface (110) of the rutile has been shown to be highly active for photocatalytic water splitting as well as for applications in the areas of catalysis and photochemistry. The surface of TiO$_2$ is like most hydrothermal crystals but not as clean as Fe$_2$O$_3$, which has a sharp surface. It is easy to identify the different elements from the EDAX mapping (Figure 3) of a single nanorod in which the green color shows that Fe of the Fe$_2$O$_3$ layer is continuously deposited on the surface of TiO$_2$ not just on the top.

![Figure 3](image)

**Figure 3.** EDAX mapping of the TiO$_2$/7 min Fe$_2$O$_3$ core/shell nanostructure by TEM.

Due to this, TEM only has one detector from one side to collect signals; the right side is brighter than the left side. The EDAX mapping from SEM (Figure S7) used here to identify large-sized nanorod arrays also showed the Fe being uniformly deposited from the top to the down-side of TiO$_2$ nanorod arrays in which the red color shows Fe and the blue color shows Ti. Also, from the EDAX mapping of SEM, the atomic amount of Fe is only 3.9% (Table S1). Both morphology and elemental analysis show that an excellent Fe$_2$O$_3$ layer with a clean surface and high-quality crystalline structure can be obtained by this PLD process, which is good for the building of the TiO$_2$/Fe$_2$O$_3$ core/shell nanostructure.

The electrochemical and optical performances for the varieties of TiO$_2$/Fe$_2$O$_3$ photoanodes with changing deposition times and TiO$_2$ photoanode are shown in Figure 5. Absorbance curves of different Fe$_2$O$_3$ deposited time samples in Figure 4a indicate that increasing the deposition time can increase the
absorption edge to absorb more visible light. The thickness of the Fe₂O₃ layer is the most important part in this nanostructure in which the thicker Fe₂O₃ layer can absorb more light, but the thinner Fe₂O₃ layer has better electrotransport performance.

Figure 4b shows the J–V curves of different Fe₂O₃ deposited times under AM 1.5G irradiation (100 mW cm⁻²). The current density increased with increasing deposition time from 1 to 7 min and then decreased at 9 min in which the very thick Fe₂O₃ layer can destroy the charge transport ability of the core/shell nanostructure due to the poor charge transport of Fe₂O₃. According to the Nernst equation

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059pH + E^0_{\text{Ag/AgCl}} \]

where \( E_{\text{RHE}} \) is the converted potential versus RHE and \( E^0_{\text{Ag/AgCl}} = 0.1976 \text{V} \) at 25 °C; the potential that is tested by the Ag/AgCl and 1 M KOH (pH ~13.6) system can be converted to the RHE system. The current density of the TiO₂/7 min Fe₂O₃ device is 0.91 mA cm⁻², and the TiO₂ device is nearly 0.55 mA cm⁻² in Figure 5a at 1.23 V versus RHE. Also, Figure 5a displays a reduced onset potential, which indicates the enhanced PEC water oxidation kinetics. The M-S measurement used here and shown in Figure S8, which displays a reduced onset potential of the TiO₂/Fe₂O₃ sample, indicates the enhanced PEC water oxidation kinetics. Generally, the conduction band (CB) of TiO₂ is (−4.1 eV) higher than that of Fe₂O₃ (−4.7 eV) and the valence band (VB) of TiO₂ is (−7.2 eV) lower than that of Fe₂O₃ (−7.0 eV) in the vacuum system.34,35 Considering the band gap of these two materials, this core/shell nanostructure may not be suitable for carrier separation and transport to react with hydroxyl. In consideration, we propose a new carrier transport theory combined with photopotential with different light wavelengths; the translucent one represents the original band gap position, and the darker one represents the band gap after photogeneration (Figure 5b).

We prepared this water splitting system with the order of light source/FTO/TiO₂/Fe₂O₃ (Figure S9) and divided the light wavelength into two parts; one is lower than 400 nm, which matches the TiO₂ band gap absorption, and one is higher for Fe₂O₃. If the light whose wavelength is lower than 400 nm came from the FTO side to TiO₂ nanorod arrays, both TiO₂ and Fe₂O₃ have photogenerated potential, and almost all light can be absorbed by the TiO₂ nanorod, which can be seen from the transmission spectrum (Figure 5c). Fe₂O₃ can still absorb a small amount of transmitted light to generate photogenerated carriers, but the small amount of photogenerated carriers in this part is difficult to transmit to the external circuit through energy band transition of TiO₂. Therefore, we think that Fe₂O₃ only reflects the conductivity of semiconductor materials in this wavelength’s water splitting process and holes can transport to Fe₂O₃ to react with hydroxyl to generate O₂. This process needs a very high quality of Fe₂O₃ films, which could transport most parts of carriers without recombination, and the thickness is also limited by the average diffusion length. If the light whose wavelength is higher than 400 nm came from FTO to the TiO₂/Fe₂O₃ core/shell structure, TiO₂ cannot absorb this part of the light, and Fe₂O₃ can absorb it. Photogenerated voltage will increase the energy band of Fe₂O₃ that is high enough to transport the photocarrier in the water splitting process, and the holes in Fe₂O₃ itself also can react with hydroxyl to get O₂. According to this inference, the thicker Fe₂O₃ layer needs a higher photogenerated voltage to transport the carrier, which is the same as the results of Figure 4b; the thicker Fe₂O₃ sample has a higher onset potential. From the curves of the transmission pattern (Figure 5c), we prepared the sample with FTO glass, a TiO₂ film, and 7 min of Fe₂O₃ directly deposited on FTO glass to check the light absorption capacity of the material itself. We can see that the cross point of two curves is 398 nm, which after that point, light can pass through the TiO₂ to Fe₂O₃. When using light/FTO/TiO₂/Fe₂O₃, almost all light whose wavelength is lower than 400 nm can be absorbed by TiO₂, only the 2 nm part could not be absorbed, and the other part of the light can be absorbed by Fe₂O₃ to get high power conversion efficiency (PCE). However, when we use the light/Fe₂O₃/TiO₂/FTO model, only the 2 nm part of the light can easily pass Fe₂O₃ to be
similar to that of the TiO$_2$ sample. However, when we order in Figure S8, the current density of the curves are shown in Figure S10. When we measured like the V$_{1.23}$ V on the black curve is about 0.45 mA cm$^{-2}$ lower than that of the light/FTO/TiO$_2$/Fe$_2$O$_3$ core/shell sample and the value of the light/Fe$_2$O$_3$/TiO$_2$/FTO order and the transmittance was measured. As seen in Figure 5d, the value of the light/Fe$_2$O$_3$/TiO$_2$/FTO sample at 1.23 V on the black curve is about 0.45 mA cm$^{-2}$ lower than that of the light/FTO/TiO$_2$/Fe$_2$O$_3$ sample and the value of the light/Fe$_2$O$_3$/TiO$_2$/FTO sample is even lower than that of the TiO$_2$ one. To further confirm this, a filter was used here to remove the wavelength that was higher than 400 nm and was put between the light source and TiO$_2$/7 min Fe$_2$O$_3$ sample; the J–V curves are shown in Figure S10. When we measured like the order in Figure S8, the current density of the filter-used sample is similar to that of the TiO$_2$ sample. However, when we illuminated from the back side with the light/Fe$_2$O$_3$/TiO$_2$/FTO order, the current density has a significant reduction.

To gain deeper insight into the charge transfer and recombination processes before and after Fe$_2$O$_3$ treatment, the EIS measurement was used here. During this measurement, both TiO$_2$ and TiO$_2$/7 min Fe$_2$O$_3$ core/shell samples were tested under AM 1.5G (Figure 6a). When samples were measured under the light model, the smaller radius of Nyquist plots meant a less recombination rate. We can see that the radius of the TiO$_2$/7 min Fe$_2$O$_3$ curve is smaller than that of the TiO$_2$ one, meaning that TiO$_2$/7 min Fe$_2$O$_3$ has a less recombination rate than TiO$_2$. We attribute this result to the clean surface and high-quality crystalline structure of a PLD-prepared Fe$_2$O$_3$ thin film, which directly contacts with the electrolyte. The Nyquist plots of Fe$_2$O$_3$ with different deposited times were measured and are shown in Figure S11 in which the 7 min sample also shows the best performance.

The stability measurement was executed over the TiO$_2$/7 min Fe$_2$O$_3$ core/shell sample for more than 1 week. From Figure 6b, we can see that the current density still remains high after 14 days of measurement and exhibits only a 3% decrease. The performance of devices even has increased after 84 h, which can be considered as temperature increased by continuous exposure.

The pristine TiO$_2$ prepared water splitting cells were also tested for 30,000 s and are shown in Figure S12, which has obviously decreased with long-time measurement. We consider that this low decay can be attributed to a high quality of a PLD-prepared Fe$_2$O$_3$ film and effective charge transport in this core/shell nanostructure. From the on/off light measurement also prepared in Figure 6c, we can see that there are nearly no peaks at the light on and light off point. This measurement also shows that the sample has good charge separation capability. The gas evolution measurement was also used here to check the products, and all electrodes are sealed in a container and connected to the gas detection device (Figure S13) and tested under AM 1.5G with 1.23 V$_{RHE}$. From Figure 6d, the rate for O$_2$ evolution is about 10.7 μmol h$^{-1}$ cm$^{-2}$ and there is no obvious decay after 70 h of testing. O$_2$ evolution is nearly the same with half the amount of holes passing through the outer circuit, which means that almost all the holes were used for water oxidation. From these analyses, the TiO$_2$/Fe$_2$O$_3$ core/shell nanostructure provides several advantages of effective light absorption, photogenerated carrier separation, and low recombination rate, thus resulting in improved PEC performance.

3. CONCLUSIONS

In summary, we designed and investigated TiO$_2$/Fe$_2$O$_3$ core/shell nanostructures as photoanodes for PEC water splitting. Due to the high-quality PLD-prepared Fe$_2$O$_3$ shell, the photocurrent density is enhanced to 0.91 mA cm$^{-2}$ under AM 1.5G, which is nearly twice as high as that of plain TiO$_2$. The effective visible light absorption, excellent carrier transport and separation, and low recombination rate synergistically contribute to the enhanced PEC water splitting performance. We hope that our findings open a promising route to design complex nanostructures by using unconventional technologies and can be universally applied in other solar energy fields.

4. EXPERIMENTAL SECTION

4.1. Preparation of Photoanodes. These photoanodes were fabricated on FTO substrates, which were washed for 30 min each with acetone, ethyl alcohol, and deionized water in an
ultrasonic bath. First, the TiO₂ nanorod arrays were prepared by a chemical hydrothermal method. Precursor solution consisted of 0.269 g of citric acid (anhydrous; Sigma-Aldrich), 1 mL of titanium(IV) butoxide (97%; Sigma-Aldrich), 30 mL of hydrochloric acid (36.5−38%; Sigma-Aldrich), and 30 mL of deionized water. A cleaned FTO substrate was immersed in the precursor of a 100 mL Teflon-lined stainless steel autoclave with the conductive side facing downward. The autoclave was put into the oven before opening the heating procedure. The autoclave was heated to 155 °C for 6 h and naturally cooled to room temperature. After the reaction process, the samples were rinsed with deionized water to remove the foreign matters deposited on the surface of the sample. Second, TiO₂/Fe₂O₃ photoanodes were prepared by the PLD (STPLD; Pascal Co. Ltd., Japan) method using Fe₂O₃ pellets (Hebei Kejing Co. Ltd., China) as targets and the prepared TiO₂ nanostructure as a substrate. The temperature for deposition was 550 °C. The chamber of the PLD machine was first evacuated lower than 10⁻⁴ Pa. For the preparation of Fe₂O₃, pure O₂ was introduced into the chamber until the pressure became 3−4 Pa. The laser was used to irradiate for different amounts of time, and we took a sample every 2 min, namely, 1, 3, 5, 7, and 9 min. After the laser irradiation, the film was kept at 550 °C for 30 min as a post-heat treatment.

4.2. Characterization. The morphology of the samples was characterized using field-emission scanning electron microscopy (FE-SEM; Hitachi, S4800) and high-resolution transmission electron microscopy (HRTEM; Jeol, JEM2100F). The phase of products was checked by X-ray diffraction (XRD, RIGAKU Rint-2000 X-ray diffractometer, Cu Kα radiation, λ = 0.15418 nm). The current density versus potential and incident photon-to-current conversion efficiency (IPCE) were measured using a WXS-80C-3 solar simulator under AM 1.5G (100 mW cm⁻²). The absorbance and transmission spectra were detected using a UV−vis spectrophotometer (Shimadzu UV-2500). Electrochemical impedance spectroscopy (EIS) and Mott−Schottky (M-S) were measured with an electrochemical workstation (ALS/CH model 650A) under light with an alternative signal (M-S) were measured with an electrochemical workstation at an AC frequency of 10⁴ Hz with an amplitude of 5 mV and a frequency range of 1.0 × 10⁻⁶ to 4.0 × 10⁵ Hz.

4.3. Photoelectrochemical Measurements. Photoelectrochemical measurements were carried out in the electrolyte containing 1 M KOH (pH ~13.6) under a three-electrode system. The work electrodes were the as-prepared FTO/TiO₂ or FTO/TiO₂/Fe₂O₃ samples, the counter electrode was a Pt sheet, and the reference electrode was a saturated Ag/AgCl electrode. Before the measurement, the inert gas Ar was used to remove the dissolved oxygen in the electrolyte for about 30 min and it was kept under the process of testing. The long-time stability and time curves with light on/off cycle measurements were performed in a closed system under simulated AM 1.5G solar illumination. The curves were recorded by scanning the potential from the negative to the positive direction with a scan rate of 0.01 V s⁻¹. M-S plots were obtained by the same workstation at an AC frequency of 10⁵ Hz with an amplitude of 5 mV under light.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02838.

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Notes
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