Introduction

Photoelectrochemical (PEC) processes offer a direct use of sunlight for a large variety of applications, including hydrogen production for energy storage, as well as hydroxyl radical formation for pollutant degradation. Among the various photocatalysts developed to date, TiO$_2$ is particularly suited to commercial scale-up because it is abundant, nontoxic, and stable under photochemical conditions. Unfortunately, its large bandgap limits its photoactivity to the ultraviolet (UV) region. As a result, in the best case it can absorb only up to 5% of incident solar photons. This limits its potential to increase further in photoelectrochemical efficiency.

Strategies to expand the TiO$_2$ optical absorption spectrum into the visible region include the sensitization of TiO$_2$ with dyes or small-bandgap semiconductors, doping, and coupling TiO$_2$ with plasmonic nanostructures. The synergistic effects of coupling TiO$_2$ with another
semiconductor include the enhancement of charge separation, visible light absorption, and photostability. Each of these properties is important for practical use in environmental applications.\cite{13,18–20} For these reasons, a variety of semiconductors such as metal oxides, metal sulfides, and metal or carbon nitrides have been used to improve the activity of TiO$_2$ in the visible region.\cite{21–25}

We took the view that the synergistic combination of TiO$_2$ with spinel ZnFe$_2$O$_4$ stands to augment photocatalytic performance considerably. Spinel ZnFe$_2$O$_4$ is a semiconductor with a bandgap of 1.9 eV that forms a type I heterostructure with TiO$_2$.\cite{26,27} It has better photochemical stability compared to other small-bandgap materials such as metal sulfides and selenides. Several approaches have been employed to synthesize ZnFe$_2$O$_4$/TiO$_2$ (ZFO/TiO$_2$) heterostructures, including electrochemical, hydrothermal, and plasma spray methods.\cite{26,28,29} These heterostructures exhibit increased photoelectrochemical performance compared to pristine TiO$_2$ electrodes.

Prior attempts have unfortunately provided limited efficiency gains. We hypothesized that the issue was an architectural one: forming of ZnFe$_2$O$_4$ nanoparticles on TiO$_2$ surface failed to offer the kinds of interfacial areas, and intimate chemical contact between the two constituent materials, required to form efficient heterojunctions.\cite{26–31} Nanoparticle-covered 1D structures exhibit relatively low multiples of sensitization, as well as suffering from a small reaction area and limited capacity for reagent diffusion for photoelectrochemical reactions.

In seeking an improved architecture, we turned to the structure of plants such as corn and sugarcane – efficient systems for the conversion of solar energy to fuels. Plants begin with 1D trunks that branch into 2D leaves that facilitate sunlight absorption. The role of the 1D portion is to improve the mass transport while the 2D is a surface-area maximizing strategy that facilitates sunlight absorption, photosynthetic reaction area, and the diffusion of reactants.\cite{32,33}

We reasoned that TiO$_2$ (1D) TiO$_2$ nanowire arrays (NWs), already available thanks to multiple prior advances,\cite{34–38} could be used as a template on top of which to grow heterostructures based on multiluminal oxide nanosheets. Unfortunately, we found that anisotropic 2D shapes are often unstable at the high temperatures, while high temperature is normally required to form a crystalline phase of mixed oxides.\cite{39} This incompatibility makes it challenging to grow 2D shaped multiluminal oxide materials.

We report herein a new synthetic route that allows the construction of ZnFe$_2$O$_4$ nanosheets on TiO$_2$ templates. Specifically, the ZnFe$_2$O$_4$/TiO$_2$ heterostructures are constructed using a combination of solution-phase materials growth techniques and completed with a final atomic layer deposition (ALD) step. The templated growth begins with the realization of FeOOH nanosheets on the surface of TiO$_2$ nanowires. These we then convert into ZnFe$_2$O$_4$ via an ensuing coating of ZnO grown by atomic ALD.

We find that the new heterostructures exhibit photoelectrochemical water splitting performance that is fully 3× higher than relevant controls under visible illumination. These results demonstrate that control over multistep multiluminal nanostructuring can enhance photoelectrochemical water splitting under sunlight.

2. Results and Discussion

2.1. Synthesis and Characterization of ZFO/TiO$_2$ Controlling the Growth of ZFO on TiO$_2$ NW

The hierarchical ZnFe$_2$O$_4$ nanosheet/TiO$_2$ nanowire structures were synthesized via a two-step approach. First, FeOOH nanosheets templates are obtained via a solution-based 2D crystal growth method. We then use atomic layer deposition of a ZnO surface layer (Figure 1A) for conversion.

In detail, TiO$_2$ nanowire arrays were synthesized on fluorine-doped tin oxide (FTO) glass substrate by a hydrothermal method.\cite{40} TiO$_2$ nanowire arrays were rinsed with $5 \times 10^{-3}$ M FeCl$_3$ solution. After 120 min sonication treatment, the shell layers have a nanosheet structure rather than being a continuous thin film shell on the surface of TiO$_2$ nanowire arrays (Figure S1, Supporting Information). These nanosheets are FeOOH per prior reports.\cite{41} The distribution of the shell nanosheets is tuned by controlling the Fe$^{3+}$ treatment time (Figure S2, Supporting Information). Subsequent to the nanosheet formation, a conformal layer of ZnO was deposited on FeOOH/TiO$_2$ heterostructures using an atomic layer deposition process. Finally, ZnFe$_2$O$_4$/TiO$_2$ heterostructures were obtained by 520°C thermal treatment and 5 M KOH immersion to remove excess ZnO (Figure S6, Supporting Information).

The morphologies of pristine TiO$_2$ nanowire arrays and ZFO/TiO$_2$ heterostructures were characterized using scanning electron microscopy (SEM). The nanowires are tetragonal in shape with square top facets and an average diameter of 30 nm (Figure 1B). Cross-sectional SEM image (Figure S3, Supporting Information) shows that pristine TiO$_2$ nanowire film consists of dense and vertically aligned nanowire arrays with a length of $\approx$5 µm. The SEM images of FeOOH/TiO$_2$ and ZFO/TiO$_2$ heterostructures are shown in Figure 1C,D. The film structure remains uniform over a large area, indicating that the nanowire arrays are intact during the growth of ZnFe$_2$O$_4$ (Figure S1B, Supporting Information). High-magnification SEM images (Figure 1E) show that TiO$_2$ nanowire arrays were uniformly covered with ZnFe$_2$O$_4$ nanosheets, forming TiO$_2$-ZnFe$_2$O$_4$ core–shell structures on the nanowires with the ZnFe$_2$O$_4$ shell having a thickness of 30–50 nm (Figure 1E). To examine the crystalline structure of ZnFe$_2$O$_4$ and TiO$_2$, we used high resolution transmission electron microscope (HR-TEM). TiO$_2$ nanowires are single-crystalline with [001] orientation (Figure 1F). The observed lattice spacing of 0.32 nm belongs to the [110] interplanar distance of rutile TiO$_2$. In addition to the pristine TiO$_2$, a crystalline structure with the lattice fringes of 0.29 nm is also present (Figure 1G), which matches well with the [220] crystallographic plane of spinel ZnFe$_2$O$_4$.

To verify the crystal structure of ZFO/TiO$_2$ heterostructures, we used X-ray diffraction (XRD), which reveals
that (Figure 2A) TiO$_2$ nanowire arrays have well-defined diffraction peaks typical of highly crystalline rutile TiO$_2$ (JCPDS 88-1175). In the XRD pattern of ZFO/TiO$_2$ heterostructures, an additional diffraction peak is present at 2$\theta$ = 30.48°, which we attribute to the (220) hkl plane of the ZnFe$_2$O$_4$ crystal structure.

To investigate the oxidation states of the metal and the surface composition in ZFO/TiO$_2$ heterostructures, we employed X-ray photoelectron spectroscopy (XPS) (Figure 2B). Two peaks in the Ti 2p XPS spectrum are present at the binding energies of 464.8 and 459.2 eV. These binding energies are in good agreement with those of Ti$^{4+}$ oxidation states in pristine rutile TiO$_2$. Compared those in pristine TiO$_2$ nanowires, the Ti 2p peaks become much weaker in the XPS spectrum of ZFO/TiO$_2$ heterostructures. This result further confirms that in the ZFO/TiO$_2$ heterostructures, ZnFe$_2$O$_4$ nanosheets cover the surface of the TiO$_2$ nanowires.

Figure 2C,D shows the Zn 2p and Fe 2p XPS spectra of Zn and Fe in ZFO/TiO$_2$ heterostructures, respectively. The two peaks appeared in the Zn 2p XPS spectra (Figure 2C) at the binding energies of 1044.4 and 1022.8 eV are characteristics of Zn 2p1/2 and Zn 2p3/2, respectively. This reveals the oxidation state of Zn$^{2+}$ in the heterostructures. In the case of Fe 2p, the two peaks located at 710.6 and 724.4 eV should be assigned to the spectra of Fe 2p3/2 and Fe 2p1/2 for Fe$^{3+}$. The Zn/Fe atomic ratio, calculated from XPS spectra is 1:2, which matches well with that in ZnFe$_2$O$_4$ material. The combination of the oxidation states and the atomic ratios confirms the presence of highly stoichiometric ZnFe$_2$O$_4$ material in the devices.

### 2.2. Controlling the Growth of ZFO on TiO$_2$ NW

To control the growth of ZFO on TiO$_2$, we systematically modified the FeOOH template by varying the treatment time of TiO$_2$ NW arrays in the Fe$^{3+}$ solution. As shown in Figure 3A, the color of ZFO/TiO$_2$ samples changes from light yellow to red orange when the treatment time increases from 60 to 180 min. This indicates that the amount of ZnFe$_2$O$_4$ loaded on ZFO/TiO$_2$ heterostructures increases with longer treatment time, which is confirmed by UV–vis absorption spectroscopy (Figure 3B). The absorption band at 600 nm, characteristic of ZnFe$_2$O$_4$ with a band gap of 2.1 eV, is also intensified with increasing treatment time, indicative of higher ZnFe$_2$O$_4$ content.

We then monitored the change in morphology of ZFO/TiO$_2$ heterostructures with different Fe$^{3+}$ treatment times (Figure 3C). Only a small amount of ZnFe$_2$O$_4$ is observed on the surface of TiO$_2$ NWs with 60 min of treatment. Extending the treatment time to 120 min resulted in large ZnFe$_2$O$_4$ nanosheets growing on the surface of TiO$_2$ NWs (Figure 3D). The slow growth rate of the nanosheets suggests that the growth of ZnFe$_2$O$_4$ stem directly from the TiO$_2$ NW surface. We propose that the higher potential energy barrier originates from the lattice mismatch between TiO$_2$ and ZnFe$_2$O$_4$ crystallites and results in slower growth kinetics of ZnFe$_2$O$_4$. After 180 min of Fe$^{3+}$ treatment, the NWs become surrounded by nanosheets as observed in Figure 3D. Blade-like ZnFe$_2$O$_4$ nanosheets emerge from the center of original TiO$_2$ NWs. ZnFe$_2$O$_4$ nucleates on preexisting nanosheets.
Figure 2. Crystallized structure and valence state of ZFO/TiO$_2$ heterostructures. A) XRD patterns of TiO$_2$ NWs (lower line) and ZnFe$_2$O$_4$ nanosheets/TiO$_2$ NWs (upper line) heterostructures. B) Ti 2p XPS spectra (TiO$^2+$ upper line), C) Zn 2p XPS spectra (TiO$^2+$ lower line), and D) Fe 2p XPS spectra of the TiO$_2$ NWs (TiO$^2+$ lower line) and ZnFe$_2$O$_4$ nanosheets/TiO$_2$ NWs heterostructures.

Figure 3. Characterization of ZFO/TiO$_2$ varying time. A) Photographs and B) UV–vis spectrum of the ZFO/TiO$_2$ heterostructures with varying Fe$^{3+}$ treatment time. SEM images of ZnFe$_2$O$_4$/TiO$_2$ heterostructures with Fe$^{3+}$ treatment C) 60 min and D) 180 min, respectively.
that, with a lower energy barrier and better epitaxy, would yield a faster reaction rate.

2.3. Photoelectrochemical Performance of TiO₂ Hybrids

To study the PEC performance of ZFO/TiO₂ heterostructures with different ZFO loadings and of pristine TiO₂ NW for water splitting, the samples were fabricated as photoanodes with a well-defined area of 1 cm². All PEC measurements were performed in a standard three-electrode electrochemical cell with a Pt wire as the counter electrode, an Ag/AgCl reference electrode, and 1 m KOH as the electrolyte solution. The reversible hydrogen electrode (RHE) potential was converted from the Ag/AgCl reference electrode as RHE = V(Ag/AgCl) + 1.0 V. Linear sweeps in a potential window between 0.2 and 1.8 V versus RHE collected for ZFO/TiO₂ heterostructures and pristine TiO₂ NW under simulated sunlight illumination at 100 mW cm⁻² is shown in Figure 4A. The pristine TiO₂ nanowire arrays exhibit a photocurrent density of 0.5 mA cm⁻² at 1.0 V versus RHE. Coupling TiO₂ NWs with ZnFe₂O₄ increases the current density of TiO₂ NWs (Figure 4A). It also can be concluded that the series resistance is lower for ZnFe₂O₄ samples while the shunt resistance remains unmodified from a function of applied potential versus RHE.

In order to investigate any benefits derived from the nanosheet structure, we synthesized ZFO/TiO₂ heterostructures in which ZnFe₂O₄ nanoparticles are grown on TiO₂ NWs nanoparticles (Figure S5, Supporting Information). As shown in Figure 4A, both ZnFe₂O₄ nanoparticles and ZnFe₂O₄ nanosheets on TiO₂ NWs heterostructures show increased photocurrent density compared to pristine TiO₂ NW arrays at 1.0 V versus RHE. The highest current density is obtained with ZFO/TiO₂ heterostructures with 120 min of sonication treatment, reaching a current density of 0.7 mA cm⁻² at 1.0 V versus RHE, which is 1.4 times higher than that of pristine TiO₂ NWs and 1.2 times higher than that of ZFO nanoparticles/TiO₂ heterostructures. Increasing the treatment time further decreases the performance of ZFO/TiO₂...
heterostructures. Longer treatment time may result in an increase of ZFO size but a constant interface area between ZFO and TiO2 NWs. The larger size of ZFO may induce charge recombination due to the short diffusion length of ZFO,[45] leading to a decrease in performance. The amount of ZnFe2O4 loaded on TiO2 affects the onset potentials of resulting ZnFe2O4/TiO2 heterostructures. With increasing amount of ZnFe2O4 nanosheets on TiO2, the onset potential is shifted to more positive potentials. This effect could be explained by the change in conduction band of ZnFe2O4/TiO2 heterostructures with varying ZnFe2O4 amount. In addition, the amount of ZnFe2O4 also affects the coverage of TiO2 nanowire surface which changes the surface activity of the heterostructure in water oxidation. This could also lead to the change in onset potential of the heterostructures.

The photoconversion efficiency $\eta$ is obtained from

$$\eta(\%) = \frac{J_p [(1.23 - V_{app})/I_0]}{J_{FCM}}$$

(1)

where $J_p$ is the photocurrent density (mA cm$^{-2}$), $I_0$ is the intensity of incident light (mW cm$^{-2}$), and $V_{app}$ is the applied potential to the photoanode (V versus RHE). Figure 4B shows the total percent photocurrent conversion efficiency $\eta$ (%) as a function of applied potential ($E_{app}$ vs RHE) for the ZFO/TiO2 heterostructures and pristine TiO2 nanowire arrays under AM 1.5. A maximum photocurrent conversion of 0.31% is obtained at an applied potential of 0.60 V versus RHE for the ZFO/TiO2 heterostructures, while it was 0.21% for pristine TiO2 nanowire arrays at 0.65 V versus RHE. The overall solar to hydrogen conversion efficiency is dependent not only on the light absorption and charge separation efficiency, but also on the catalytic activity of the electrodes. In this case, the catalytic activity of water oxidation on ZnFe2O4 limit the overall water splitting efficiency. This could be enhanced by coupling the photoanode heterostructure with superior water oxidation catalyst.

We then sought to investigate the effect of ZFO loading on the photoelectrochemical performance of TiO2 NWs under visible light irradiation by applying a 420 nm cut-off filter to remove the fraction of the UV light of the simulated solar spectrum. The data (Figure 4C) reveal that ZFO/TiO2 shows a much higher performance compared to pristine TiO2 NWs under visible light illumination. At 1.0 V versus RHE, ZFO/TiO2 heterostructures exhibit a current density of 0.18 mA cm$^{-2}$. This value is fully three times higher than that of pristine TiO2 NWs (0.06 mA cm$^{-2}$). The photocurrent on ZFO/TiO2 under 1.5 AM solar obtained with back side illumination is slightly higher than that obtained with front side illumination. This result could be explained by the fact that the TiO2 is the main contribution to the photocurrent density of ZFO/TiO2 heterostructures. The ZFO on the top of TiO2 NW array could reflect the UV light when illuminating from the front, leading to a slight decrease in overall performance of ZFO/TiO2.

To study the chemical and structural stability during PEC water splitting, we carried out time-dependent measurement on ZFO/TiO2 heterostructures and TiO2 NWs as shown in Figure 4D. The rise and fall of the photocurrent correspond well to the illumination being switched on and off. When the illumination was interrupted, the current rapidly dropped to almost zero. Upon illumination, the photocurrent reverted to the original steady state value within a couple of seconds (>90% of the steady state value was obtained instantaneously). The ZFO/TiO2 heterostructures show a highly stable photocurrent density of ~0.2 mA cm$^{-2}$ versus 1.2 V RHE with repeated on/off cycles under visible light over the course of 300 s. This result implies that the formation of a heterojunction between ZFO and TiO2 increases the separation of photogenerated holes and electrons which prolong the lifetime of generated charges, leading to a higher photocatalytic activity compared to pristine TiO2 nanowires. These data suggest that with the high activity and potential long-term stability, ZFO/TiO2 heterostructures could be ideal for visible light driven photoelectrocatalysis.

The mechanism for the enhancement in PEC performance of ZFO/TiO2 heterostructures compared to TiO2 NWs is illustrated in Figure 5. Ultraviolet photoelectron spectroscopy (UPS) indicates the work function and valence band maximum level of TiO2 and ZnFe2O4 confirming a type II band alignment in TiO2/ZnFe2O4 heterostructures (Figure 5A,B). The overall conversion process is depicted as follows: ZFO is excited by incident light and generates electron–hole pairs (step 1), and electrons in the conduction band of ZnFe2O4 are transferred to conductive FTO though TiO2 NWs (step 2). At the same time, the holes in the valence band of ZnFe2O4 oxidize H2O to O2 (step 3). The charge separation between TiO2 NWs and ZnFe2O4 enhances photoelectrochemical performance under solar and visible light illumination. 2D ZnFe2O4 with large surface area exposed also contribute to performance of ZFO/TiO2 heterostructures.

3. Conclusion

We report herein a sequential pathway to the materials synthesis of 2D/1D multimetal oxide nanosheets/TiO2 nanowire heterostructures. We achieved this by depositing the nanosheets with a mixture of metal oxide precursors using a solution phase method followed by an ALD-based cation introduction. We demonstrate an application of these new materials enabled by growing ZnFe2O4/TiO2 heterostructures involving an initial growth of FeOOH nanosheets template on TiO2 NWs, which we subsequently convert into ZnFe2O4 by ZnO ALD deposition and thermal treatment. Our 2D/1D ZnFe2O4/TiO2 heterojunctions exhibit 1.4 and three times higher photoelectrochemical performance compared to that of pristine TiO2 NWs under solar and visible light illumination, respectively. The 2D/1D ZnFe2O4/TiO2 heterostructures form a material system that enhances photoelectrochemical water splitting. The strategy may be extended to other mixed-metal oxide nanosheets systems having applications in catalysis, energy storage, and conversion.

4. Experimental Section

Materials: Iron (III) chloride (FeCl3) and titanium isopropoxide (99% Aldrich) were purchased from Sigma-Aldrich. All the chemicals were used without further purification.
Synthesis of TiO₂ Nanowire Arrays on FTO Substrate: In a typical process, the FTO substrates were first cleaned with a mixture of isopropanol and water for 2 h under sonication condition and were then dried with N₂ gas at room temperature. To a mixture of deionized water (15 mL) and hydrochloric acid (15 mL, 36.5 wt%), was added titanium isopropoxide (0.45 mL, 99% Aldrich) under stirring condition. After 1 h of stirring, the mixture was transferred to a Teflon-lined stainless steel autoclave. Cleaned FTO/glass substrates (2 cm × 2 cm) were immersed into the water/HCl/titanium isopropoxide mixture with the conducting side face down. The autoclave was put in an oven set at a temperature of 160 °C and was taken out from the oven after 5 h of crystallization. The autoclave was cooled down to room temperature and the TiO₂ NWs grown on FTO substrate were washed several time with ethanol and DI water and were subsequently annealed at 450 °C in air for 1 h.

Synthesis of 2D/1D ZnFe₂O₄ Nanosheets/TiO₂ Nanowires Heterostructures: The annealed TiO₂ nanowire arrays substrate were immersed into 5 × 10⁻³ M FeCl₃ aqueous solution. The mixture was then sonicated for different time. The obtained FeOOH/TiO₂ composite were cleaned with isopropyl alcohol and DI water followed by a drying step with N₂ gas. ZnO layer was deposited on the surface of FeOOH/TiO₂ by ALD technique using diethylzinc (99.90%, Strem) and pure DI water as the precursors. 50 cycles of ALD were used to produce ZnO layer with a thickness of 10 nm. Finally, ZnFe₂O₄/TiO₂ heterostructures were obtained by annealing ZnO/FeOOH/TiO₂ at 520 °C for 3 h followed by a treatment with 5 M KOH solution to remove excess ZnO.

Characterization: Surface SEM and cross-section SEM of TiO₂ nanowires and ZnFe₂O₄/TiO₂ heterostructures were taken on a Hitachi SU8230 scanning electron microscope operated at 1.0 kV. Transmission electron microscopy (TEM) and HRTEM images of the samples were prepared on carbon-coated copper TEM grids (Ted Pella, Redding, CA) using micropipettes and were dried under ambient condition. Powder XRD patterns were obtained with MiniFlex600 instrument. Data was collected in Bragg-Brentano mode using 0.02 ° divergence with a scan rate of 0.1 ° s⁻¹. XPS measurements were carried out in a Thermo Scientific K-Alpha system, with a 300 µm spot size, 75 eV pass energy, and energy steps of 0.05 eV, aluminum anode X-ray excitation. UPS spectra were performed in a PHI5500 Multi-Technique system using nonmonochromatized He-Iα radiation (UPS, hν = 21.22 eV). All work function and valence band measurements were performed at a take-off angle of 88°, and the chamber pressure was ≈10⁻⁹ torr. Work functions (WF) were calculated from the secondary electron cut-off (SEC) using the equation WF = 21.22 eV – SEC. The differences between Fermi levels and valence band maximum, η, were determined from the low binding energy onset. The absorbance of the samples has been obtained by gas chromatography (PerkinElmer Clarus 680) equipped with Molecular sieve 5A capillary column and thermal conductivity detector (Figure S8, Supporting Information).
Photoelectrochemical Measurement: Photoelectrochemical measurements were performed using a three-electrode system connected to an electrochemical workstation (Autolab PGSTAT302N) in 1 mM KOH electrolyte. ZnFe$_2$O$_4$/TiO$_2$ electrode were used as the working electrode (photoanode). Ag/AgCl (saturated KCl) electrode and Pt wire were used as reference electrode and counter electrode, respectively. Photocurrent versus voltage (I–V) characteristics were recorded from −1 V to +1 V with a scan rate of 1 mV s$^{-1}$. All experiments were performed at ambient temperature (22 °C ± 2 °C) and electrode potentials were converted to the RHE scale using $E$(RHE) = $E$(Ag/AgCl) + 0.197 V + 0.059 × pH. Where $E$(RHE) is the converted potential versus RHE, and $E$(Ag/AgCl) is the measured potential versus Ag/AgCl reference electrode. Transient photocurrent density versus time plots of TiO$_2$ and ZnFe$_2$O$_4$/TiO$_2$ heterostructures were recorded at an applied potential of 1.2 V versus RHE under visible light sources.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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