A New WO$_3$/FeVO$_4$ Nanostructured Heterojunction for Solar-driven Water Oxidation

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Abstract. We report the first application of a nanostructured WO$_3$/FeVO$_4$ heterojunction to photoelectrochemical (PEC) water oxidation. The heterojunction films were prepared by drop-casting a low bandgap (~2.1 eV) FeVO$_4$ layer onto a wider bandgap (~2.8 eV) WO$_3$ nanoporous film supported on a fluorine-doped tin oxide coated glass substrate. The structural, optical and PEC properties of the prepared heterojunction were analysed in detail, and it was found that the WO$_3$/FeVO$_4$ composite reached maximum photocurrent densities under simulated sunlight up to 3.3 and 12 times higher than those of pristine WO$_3$ and FeVO$_4$ photoanodes, respectively. A large and desirable ~400 mV cathodic shift in the photocurrent onset potential relative to pristine FeVO$_4$ was also observed, which can be attributed to lower surface recombination and more efficient bulk separation of photogenerated electron–hole pairs compared with both pristine FeVO$_4$ and WO$_3$. These findings suggest that WO$_3$/FeVO$_4$ nanostructured heterojunctions may find applications in solar-driven water splitting cells.

1. Introduction
Photoelectrochemical (PEC) water splitting is an environmentally friendly and sustainable process to produce hydrogen by converting solar energy directly into chemical energy using semiconductor photoelectrodes [1]. Various semiconducting oxides such as TiO$_2$ [2], WO$_3$ [3], and BiVO$_4$ [4] have drawn much attention for use as PEC photoanodes in recent decades, but because of their comparatively wide bandgaps these materials do not effectively utilise all of the incident solar energy. In this regard, FeVO$_4$ is an intriguing photoanode material among the other metal oxide semiconductors that absorb visible light owing to its reasonably good chemical stability, natural abundance of raw materials [5], and low cost [6]. The ~2.1 eV indirect bandgap makes it sensitive to visible light up to a wavelength of ~600 nm, and its valence band edge energy is ideal for water oxidation [7]. However, several issues including sluggish charge carrier transport together with excessive photoinduced electron–hole pair recombination and poor water oxidation kinetics still restrict the PEC performance of unmodified FeVO$_4$ [5]. Much recent research has shown that coupling semiconductor materials to form heterojunctions can result in significant increases in PEC activity. Each participating material in the heterostructure possesses different properties such as high absorption coefficient, fast charge transport, or enhanced photostability that combine to benefit the overall PEC reaction [8].
In this study, we paired FeVO$_4$ (with good light absorption properties) and WO$_3$ (with fast charge transport) [9] to create a nanostructured heterojunction, with the goal of simultaneously improving light absorption, interfacial charge separation, and majority carrier transport. There are so far no reports of photoanodes based on WO$_3$/FeVO$_4$ heterojunctions in the literature, and this report discloses their PEC properties for the first time. Compared with pristine WO$_3$, the WO$_3$/FeVO$_4$ photoanode exhibited 3.3 times higher water oxidation photocurrent density under simulated 1 Sun (AM1.5G, 100 mW cm$^{-2}$) illumination at 1.2 V vs. RHE, without any sacrificial agent or cocatalyst loading. Measurements made with a sacrificial hole scavenger reveal that the FeVO$_4$/WO$_3$ photoanode has greatly enhanced surface charge transfer efficiency compared with either of the pristine oxides, indicating that the heterojunction itself plays an important role in mitigating charge recombination.

2. Experimental

WO$_3$/FeVO$_4$ heterojunctions on fluorine-doped tin oxide (FTO)-coated glass substrates were prepared by simple and cost-effective spin-coating and drop-casting of the individual materials. Commercially available WO$_3$ powder (Sigma-Aldrich; <100 nm particle size) was used to make a paste following a procedure adapted from Ito et al. [10]. The desired amount of paste was then spin-coated at 1000 rpm for 60 sec on clean FTO (1 cm $\times$ 3 cm area) to obtain an optimized thickness of WO$_3$. The films were initially dried at 100 °C on a hot plate for 10 minutes followed by annealing in a furnace at 600 °C for one hour. An FeVO$_4$ coating was deposited on the nanoporous WO$_3$ film by drop-casting 200 µl of an aqueous precursor solution with the following composition: 0.01 M Fe(NO$_3$)$_3$·9H$_2$O, 0.01 M NH$_4$VO$_3$, 0.01 M citric acid, and 2 M HNO$_3$. The precursor-coated WO$_3$ was dried at 75 °C on a hot plate for 30 min then annealed at 600 °C for one hour. Pristine WO$_3$ and FeVO$_4$ films were also prepared by the same spin-coating and drop-casting methods, respectively.

3. Results and discussion

The crystallographic properties of the photoanodes were examined by X-ray diffraction (XRD) using a Shimadzu XRD 7000 diffractometer (Figure 1a). The XRD patterns for commercial WO$_3$ (not shown) and WO$_3$/FeVO$_4$ photoanodes match well with orthorhombic WO$_3$ (PDF# 20-1324), and the pattern for the pure FeVO$_4$ photoanode matches triclinic FeVO$_4$ (PDF# 38-1372). No clear FeVO$_4$ diffraction peaks can be detected in the pattern of the WO$_3$/FeVO$_4$ composite film; however, optical transmittance and reflectance measurements clearly indicate the presence of FeVO$_4$ in these samples, as expected from the synthesis. A possible reason for the lack of detection in the XRD measurements is that the FeVO$_4$ is highly dispersed on the surface of the WO$_3$ nanoparticles, as reported for other heterojunction films prepared by similar methods [11].

![Figure 1. X-ray diffraction patterns of the prepared FeVO$_4$ and WO$_3$/FeVO$_4$ photoanodes (a), and scanning electron micrographs of the WO$_3$ scaffold before (b) and after (c) coating with FeVO$_4$.](image)

The morphologies of the pristine WO$_3$ (Figure 1b) and WO$_3$/FeVO$_4$ (Figure 1c) films were observed using a JEOL JSM-7600F scanning electron microscope. Slight decreases in porosity and...
film thickness are observed after the deposition of FeVO₄, which indicates that the FeVO₄ penetrates into the porous WO₃ film to form a nanostructured heterojunction and does not simply form a planar overlayer.

The light-harvesting efficiency (LHE) spectra (Figure 2a) of the prepared photoanodes were calculated from transmittance and reflectance spectra measured using a Thorlabs CCS200 spectrometer coupled to an integrating sphere with a xenon light source. The WO₃ film has lower LHE across almost the entire wavelength range due to the indirect nature of its relatively wide bandgap (~2.8 eV), whereas the FeVO₄ film has mostly higher LHE and a longer wavelength absorption onset owing to its direct (~2.6 eV) and indirect (~2.1 eV) bandgaps [12]. The LHE of the WO₃/FeVO₄ composite is higher than that of the two individual components at all wavelengths, indicating that incorporation of FeVO₄ into the WO₃ film increased the overall LHE, as expected.

Figure 2. Light harvesting efficiency spectra (a), current density–potential characteristics under 1 Sun illumination (b), IPCE spectra (c), and complex impedance plots (d) of the WO₃, FeVO₄ and WO₃/FeVO₄ photoanodes.

The PEC water oxidation performance of the WO₃, FeVO₄ and WO₃/FeVO₄ photoanodes was evaluated by measuring current density–potential (J–E) characteristics under 1 Sun illumination in 0.5 M Na₂SO₄ electrolyte (Figure 2b). The WO₃/FeVO₄ photoanode showed improved activity compared with either pristine material, with ~400 mV earlier photocurrent onset than pristine FeVO₄ and a photocurrent density of 0.7 mA cm⁻² at 1.2 V vs. RHE, around 3- or 12-times greater than WO₃ (0.23 mA cm⁻²) or FeVO₄ (0.06 mA cm⁻²), respectively. The improvement in photocurrent is even more pronounced at higher potentials, reaching over 2 mA cm⁻² at 1.8 V vs. RHE. Recently, Wu et al. investigated the influence of a TiO₂ underlayer on the PEC properties of FeVO₄ photoanodes. Their FeVO₄/TiO₂/FTO photoelectrode achieved a photocurrent density of 0.35 mA cm⁻² at 1.6 V vs. RHE, which is ~35% higher than the FeVO₄/FTO photoelectrode (0.26 mA cm⁻²) and had an IPCE of 17% at 350 nm, compared to 10% for unmodified FeVO₄. According to these authors, the ultrathin TiO₂
The interfacial layer acts as a hole blocking layer, preventing back hole transfer from FeVO₄ to FTO and thus lowering charge recombination [13]. However, in our study we believe that the increase in photocurrent can mainly be attributed to improved photogenerated electron–hole separation in the bulk of the WO₃/FeVO₄ composite because we observed increasing photocurrent with increasing WO₃ layer thickness (data shown are for an optimised layer thickness of ~1 μm).

To determine the maximum achievable photocurrent from these photoanodes and probe the extent of surface recombination, sulfite oxidation experiments were performed. In a typical experiment, 0.25 M Na₂SO₃ was added to the electrolyte solution and the surface charge transfer efficiency ($\eta_{ct}$) was determined using

$$\eta_{ct} = \frac{J_{H_2O}}{J_{sulfite}}$$

where $J_{H_2O}$ and $J_{sulfite}$ are the photocurrent densities in the absence and presence of Na₂SO₃, respectively. At 1.2 V vs. RHE, $\eta_{ct}$ for the WO₃/FeVO₄ photoanode (76%) is over 2 times higher than for pristine WO₃ (37%), which explains almost two-thirds of the enhancement in photocurrent, the remainder being attributable to the enhanced LHE of the composite. Interestingly, pristine FeVO₄ also suffers from inefficient charge transfer ($\eta_{ct} = 57\%$), so the enhanced $\eta_{ct}$ of the composite cannot solely be attributed to the FeVO₄ surface being more catalytic for water oxidation than the WO₃ surface. These findings indicate that the enhancement in $\eta_{ct}$ likely arises from the formation of a heterojunction between WO₃ and FeVO₄, which improves electron–hole pair separation near the surface.

The incident photon-to-current efficiency (IPCE) spectra of the WO₃, FeVO₄, and WO₃/FeVO₄ photoanodes were measured for comparison with the LHE (Figure 2c). The WO₃/FeVO₄ photoanode produced measurable photocurrent up to ~500 nm, and most of the light absorption comes from FeVO₄ above ~450 nm. The peak IPCE for WO₃/FeVO₄ (54%) is about 3 or 4 times greater than that of the pristine WO₃ (18%) or FeVO₄ (4%) photoanodes, respectively, which is consistent with the above J-E results. The large relative improvement in peak IPCE, which is much greater than the relative improvement in LHE (~10%), suggests that photogenerated holes are more effectively transferred to the semiconductor–solution interface in the WO₃/FeVO₄ photoelectrode [9].

The interfacial charge transfer properties of the WO₃/FeVO₄, FeVO₄, and WO₃ photoanodes were further examined using electrochemical impedance spectroscopy at an applied potential of 1.2 V vs. RHE under 0.1 Sun illumination. The EIS spectra (Figure 2d) were fitted using a Randles circuit (inset of Figure 2d) to extract the series and charge transfer resistances ($R_s$ and $R_{ct}$) and interfacial capacitance (C) [14]. The $R_{ct}$ value of the WO₃/FeVO₄ composite electrode is 7.3 kΩ cm², which is much lower than that of pure WO₃ (54 kΩ cm²) or FeVO₄ (12 kΩ cm²), showing that charge transfer becomes more facile after incorporation of FeVO₄.

The stability of the WO₃/FeVO₄ photoelectrode was evaluated by monitoring the normalised photocurrent at 1.2 V vs. RHE for 1 hour under 1 Sun illumination (Figure 3). For comparison, the same experiment was performed for a pristine WO₃ photoelectrode. It is evident that addition of FeVO₄ greatly improves the photostability of the underlying WO₃, with no drop in photocurrent after 1 hour for the composite compared with a 34% drop for uncoated WO₃. These findings show that heterojunction formation not only suppresses recombination and improves carrier transfer at the electrode surface but also significantly improves stability, which is a further advantage of the novel WO₃/FeVO₄ heterojunction reported here.
Figure 3. Stability of uncoated WO₃ and the new WO₃/FeVO₄ nanocomposite monitored by normalised current density ($J/J_0$) at 1.2 V vs. RHE under 1 Sun illumination. The higher noise and steps in the data for WO₃/FeVO₄ are due to increased bubble formation during water oxidation.

4. Conclusion
In summary, a new WO₃/FeVO₄ nanostructured heterojunction photoanode has been prepared and evaluated for PEC water splitting applications. A remarkable synergistic effect between WO₃ and FeVO₄ was observed, with about 3.3 times higher photocurrent being achieved compared with pristine WO₃. About two-thirds of this improvement can be attributed to increased $\eta_c$, with the rest being due to improved LHE. Interestingly, $\eta_c$ for the WO₃/FeVO₄ composite is significantly larger than those of both WO₃ and FeVO₄, which suggests that the heterojunction is close enough to the surface to alter the relative rates of surface charge transfer and recombination. We expect these findings will increase interest in using heterojunction formation as a strategy to improve the PEC performance of FeVO₄ and related materials.

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