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Simultaneously Efficient Light Absorption and Charge Separation in WO₃/BiVO₄ Core/Shell Nanowire Photoanode for Photoelectrochemical Water Oxidation

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Abstract

We report a scalably-synthesized WO₃/BiVO₄ core/shell nanowire photoanode in which BiVO₄ is the primary light-absorber and WO₃ acts as an electron conductor. These core/shell nanowires achieve the highest product of light absorption and charge separation efficiencies among BiVO₄-based photoanodes to date and, even without an added catalyst, produce a photocurrent of 3.1 mA/cm² under simulated sunlight and an incident photon-to-current conversion efficiency of ~60% at 300-450 nm, both at a potential of 1.23 V vs. RHE.

Simultaneously Efficient Light Absorption and Charge Separation in WO₃/BiVO₄ Core/Shell Nanowire Photoanode for Photoelectrochemical Water Oxidation

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Photoelectrochemical (PEC) water-splitting produces hydrogen using solar energy and is an example of artificial photosynthesis, by which the energy of sunlight is converted to chemical fuels.^{1, 2} Due to the large voltage required for water-splitting and the desirability of small band gaps for efficient light absorption, a two-electrode tandem system in which a photocathode and photoanode are connected in series and the water-splitting reaction is divided into two half reactions, promises to be more efficient than a single semiconductor system.²⁻⁵ However, the efficiency of these proposed tandem systems is presently limited by the low photocurrents achieved by the oxygen-evolving photoanodes.^{6, 7} Metal oxides, due to their stability under oxidizing conditions,^{8, 9} have been heavily researched as materials for the photoanode. However, the commonly-studied binary oxides TiO₂^{10, 11} and WO₃¹² have band gaps that are too large to absorb light efficiently (~ 3.0 and ~ 2.6 eV, respectively), while the commonly studied Fe₂O₃, despite its desirable band gap of ~ 2.2 eV, has a conduction band edge at 0.55 V vs. the reversible hydrogen electrode (RHE),¹³ which is further from the vacuum level than desired for a PEC photoanode, and extremely poor charge transport properties which have prevented efficient charge separation.¹⁴⁻¹⁶

Recently, the ternary oxide BiVO₄ has become the top-performer amongst all metal oxide photoanodes due to its relatively small bandgap of 2.4 eV which permits efficient light absorption, its relatively negative conduction band edge (~ 0 V vs. RHE), and moderate charge transport properties.^{6, 17, 18} Theoretically, the maximum water oxidation photocurrent (J_{max}) for BiVO₄ photoanodes under Air-Mass 1.5 Global (AM 1.5G) solar illumination is 7.5 mA/cm².¹⁷ Nevertheless, the practical water oxidation photocurrent (J_{H_2O}) is much lower due to the limited light absorption, charge separation and surface charge transfer efficiencies (η_{abs} , η_{sep} and η_{trans} , respectively) of the BiVO₄ material, according to $J_{H_2O} = J_{max} \times \eta_{abs} \times \eta_{sep} \times \eta_{trans}$.^{13, 19, 20} Various efforts have been devoted to increase these efficiencies. Specifically, the charge transfer efficiency η_{trans} has been dramatically improved by coating oxygen evolution reaction (OER) catalysts onto the BiVO₄ surface for improving the water oxidation kinetics and/or passivating surface defects.^{6, 18, 19, 21-29} The charge separation efficiency η_{sep} of BiVO₄ has been improved by a range of methods, including introduction of nanoscale porosity,^{6, 19, 21, 22, 24, 26, 27, 30,} reduction of BiVO₄ thickness,^{6, 25} introduction of electron-donating dopants such as Mo and W,^{6, 19, 22, 27, 32-35} and formation of a distributed homojunction by the introduction of a gradient doping concentration of W in a BiVO₄ film.¹⁸ Moreover, η_{sep} has also been improved by the

formation of heterojunctions of BiVO₄ with other materials including films (SnO₂,^{18, 25, 36-38} SiO₂,³⁹ WO₃,^{35, 40-42} graphene⁴³ and others^{44, 45}) and nanowires (WO₃^{46, 47} and Fe₂O₃⁴⁸). Amongst the latest state-of-the-art BiVO₄-based photoanodes, the highest efficiency was achieved by a W-doped BiVO₄ film with gradient doping of W and an underlying SnO₂ heterojunction, synthesized on a textured substrate, and coated with cobalt phosphate (CoPi) OER catalyst, for which η_{abs} , η_{sep} and η_{trans} were reported at the reversible water oxidation potential of 1.23 V vs. RHE as 75%, 60% and nearly 100%, respectively.¹⁸ Though η_{trans} at 1.23 V vs. RHE has approached nearly 100% by the use of OER catalysts, the achieved $\eta_{abs} \times \eta_{sep}$ product is only 45% because the hole and electron diffusion lengths are shorter than the light absorption depth.^{6, 19, 25, 37} Hence, achieving simultaneously high η_{abs} and η_{sep} remains a challenge and needs to be addressed in order to realize high performance BiVO₄ photoanodes for PEC water oxidation.

In this study, we demonstrate a photoanode that achieves the highest reported $\eta_{abs} \times \eta_{sep}$ product (53%) among BiVO₄-based photoanodes by coating a thin layer of BiVO₄ onto a vertical array of electrically conductive WO₃ nanowires (NWs) to form WO₃/W-doped BiVO₄ core/shell NWs (WO₃/W:BiVO₄ NWs, Fig. 1a). In this structure, BiVO₄ is the primary light-absorber and WO₃ acts as an electron conductor. Such core/shell NWs successfully incorporate all the previously mentioned strategies for enhancing charge separation in BiVO₄, including thickness reduction, introduction of nanoscale porosity, heterojunction formation and gradient doping, into a single structure. In addition, they permit efficient light absorption by orthogonalizing the directions of light absorption and charge transport in BiVO₄ and further improve charge separation by providing a conductive pathway through the WO₃ NW cores for electrons to reach the current collector. Though a WO₃/BiVO₄ core/shell nanorod photoanode⁴⁶ and a WO₃ NW/BiVO₄ heterojunction photoanode⁴⁷ have been attempted before, the efficiency of the present WO₃/W:BiVO₄ NW photoanodes is higher because of superior morphology which simultaneously optimizes light absorption and charge transport. In the following, we will describe the synthesis and characterization of the present WO₃/W:BiVO₄ NWs in detail and explain the origin of the improved PEC performance.

The WO₃/W:BiVO₄ NWs were synthesized by a combination of flame vapor deposition and drop-casting. First, flat fluorine-doped tin oxide (FTO) substrates (2.5 x 1.7 cm, 2.3 mm thick, 8 Ω/\square , Hartford Glass) were cleaned and completely coated with a layer of 70-100 nm-thick tungsten oxide by spin-coating, in order to promote uniform and dense nucleation of the NWs.⁴⁹ Next, crystalline substoichiometric W₁₈O₄₉ NWs were synthesized on the coated FTO substrates via atmospheric flame vapor deposition at a substrate temperature of 550 °C for 30 minutes, as reported in our previous work.⁴⁹⁻⁵² This flame-synthesis method is rapid, economical and scalable, which is important for practical applications. The as-grown W₁₈O₄₉ NWs were further annealed in air at 550 °C in a box furnace for 2 hours, after which stoichiometric WO₃ NWs were obtained (Fig. 1b). Next, a solution containing 50 mM bismuth and 46.5 mM vanadium prepared by dissolving bismuth nitrate pentahydrate (98%) and vanadyl acetylacetonate (98%) in 20:1 (v/v) acetic acid (99.7%): acetyl acetone (99%) was coated onto the WO₃ NWs by drop-casting. 6 coats of the solution, in total, were applied to each sample. For each coat, 20 μ L was dropped on the sample, which was allowed to dry at room temperature and

then briefly annealed on a hotplate at 450 °C for 2 minutes. Finally, after all the coating steps, the samples were annealed in air at 550 °C in a box furnace for 2 hours to yield a crystalline W-doped BiVO₄ shell composed of a single layer of densely packed nanoparticles on the WO₃ NWs (Fig. 1c). Here, W was naturally doped into BiVO₄ during the annealing process because of the intimate contact of WO₃ and BiVO₄ in the core/shell structure, as will be described next.

The morphologies, crystal structures and chemical composition of the WO₃/W:BiVO₄ core/shell NWs were characterized by scanning electron microscopy (SEM, FEI Sirion XL30, 5 kV), parallel beam X-ray diffraction (XRD, PANalytical XPert 2, Cu-K α , 45 kV, 40 mA), transmission electron microscopy (TEM, FEI Tecnai G2 F20 X-TWIN FEG, 200 kV) and TEM-energy dispersive X-ray spectroscopy (TEM-EDS). Monoclinic WO₃ and monoclinic W:BiVO₄ are the only phases detected in XRD measurements (Fig. 2a). The XRD pattern of the WO₃ NWs is nearly unchanged after adding the W:BiVO₄ shell and the average W doping in the W:BiVO₄ shell is approximately 7%, as estimated from the magnitude of the shift of the W:BiVO₄ XRD peaks from those of undoped BiVO₄ (Supporting Information Fig. S3).^{19, 32, 33} It is known that W⁶⁺ dopes into BiVO₄ by substituting for V⁵⁺, and acts as an electron donor.³² For this reason, the Bi-V drop-casting solution was formulated to contain Bi:V = 100:93, with 7% W-doping coming from the WO₃ NWs. In addition, the TEM-EDS (Fig. 2b) clearly shows that there is considerable inter-diffusion of the elements across the core/shell interface, and the sum of the V and W concentrations is approximately equal to the Bi concentration in the shell, as would be expected for W-doped BiVO₄. Moreover, there is a concentration gradient of W in the BiVO₄ shell, with the highest W concentration near the WO₃ core and decreasing W concentration across the shell. The best-performing photoanode consists of WO₃ NWs with average lengths of 2.5 μ m, average diameters of 75 nm and average inter-wire spacing of 350 nm, coated with a W:BiVO₄ layer of 60 nm average thickness (see Supporting Information Fig. S1 and S2 for additional SEM images and a histogram of NW diameters).

The PEC performance of the WO₃/W:BiVO₄ core/shell NW photoanode (masked to expose an illuminated area of 0.63 cm²) was evaluated by measuring the current density-voltage (*J-V*) curve and incident photon-to-current conversion efficiency (IPCE) plot under electrolyte-side illumination (as shown in Fig. 1a) in aqueous 0.5 M potassium phosphate solution that is buffered to pH 8. The electrochemical measurement was performed in a three-electrode configuration with the photoanode as the working electrode, a saturated calomel (SCE) reference electrode, and a Pt wire (0.8 mm² surface area) as the counter electrode, using a potentiostat (Model SP-200, BioLogic). Potentials are reported vs. RHE using $V \text{ vs. RHE (volt)} = V \text{ vs. SCE (volt)} + [0.059 \text{ (volt)} \times \text{pH}] + 0.244 \text{ (volt)}$. *J-V* curves were measured at a scan rate of 50 mV/sec, under illumination from a class-AAA solar simulator (Model 94063A, Oriel), with the total intensity measured by a calibrated silicon solar cell and readout meter (Model 91150V, Newport). Although it is common to simply use an overall illumination intensity of 100 mW/cm² for *J-V* measurements, this can introduce errors because of the significant spectral mismatch between the AM 1.5G standard and the lamp output. Therefore, to ensure that the illumination closely simulates the AM 1.5G standard, we measured the spectral irradiance of the illumination at the sample location using a spectrometer (Ocean Optics) and adjusted the overall intensity to

85 mW/cm² to achieve the desired 7.5 mA/cm² integrated photon current up to the 515 nm band-edge wavelength of BiVO₄ (illumination spectrum at sample is provided and compared to AM 1.5G spectrum in Supporting Information Fig. S4). IPCE was measured at 1.23 V *vs.* RHE using a 75 W Xe lamp equipped with a monochromator (CM-110, 1/8 m, Spectra Products). The incident light intensity at each wavelength was measured by a calibrated silicon photodiode, and is given in Supporting Information Fig. S4. The IPCE was calculated from $IPCE (\%) = [J_{ph} (\text{mA}/\text{cm}^2) \times 1240 (\text{volt} \times \text{nm})] / [P_{mono} (\text{mW}/\text{cm}^2) \times \lambda (\text{nm})] \times 100\%$, where J_{ph} is the photocurrent density, P_{mono} is the intensity of the incident monochromatic light, and λ is the wavelength of the monochromatic light.²⁰ During all J - V and IPCE measurements, the electrolyte was purged with Ar to remove dissolved oxygen and prevent signals from oxygen reduction.

The photocurrent of the WO₃/W:BiVO₄ core/shell NWs (J - V curve in Fig. 3a) reaches 3.1 mA/cm² at a potential of 1.23 V *vs.* RHE under the simulated AM 1.5G illumination, and closely matches the photocurrent of 3.0 mA/cm² obtained by integrating the measured IPCE (Fig. 3b) over the standard AM 1.5G spectrum. These photocurrent values of the WO₃/W:BiVO₄ NWs without the addition of OER catalysts are quite close to that achieved at the same potential by the best-performing W-gradient doped BiVO₄ photoanode with an OER catalyst added for which, although a value of 3.6 mA/cm² was reported at 1.23 V *vs.* RHE under simulated illumination, a value of ~3.4 mA/cm² is obtained by multiplying J_{max} (7.5 mA/cm²) by the reported η_{abs} of 75% and the reported η_{sep} of 60% at 1.23 V *vs.* RHE, even if η_{trans} = 100%.¹⁸ Apart from that best-performing W-gradient doped BiVO₄ photoanode, for which IPCE was not reported, the average IPCE of our WO₃/W:BiVO₄ core/shell NWs over the 300-450 nm range at 1.23 V *vs.* RHE is about 60%, which is the highest for any BiVO₄-based photoanode at this potential, including those with added OER catalysts.^{6, 19, 26, 27, 40, 42, 47}

To evaluate possible synergistic effects between WO₃ and W:BiVO₄ in the core/shell NWs, J - V curves (Fig. 3a) and IPCEs (Fig. 3b) were also measured for the bare WO₃ NW array and a porous 1.5 μm -thick 7% W-doped BiVO₄ film containing the same mass of Bi as that in the core/shell NWs (hereafter referred to as the ‘same-mass W:BiVO₄ film’, SEM images provided in Supporting Information Fig. S1). 7% W-doping was chosen because it matches the average doping level in the W:BiVO₄ shell of the WO₃/W:BiVO₄ NWs. The same-mass W:BiVO₄ film was prepared by drop-casting a solution containing B:V:W = 100:93:7 onto bare FTO glass, with drop-casting and subsequent annealing steps identical to those used for the WO₃/W:BiVO₄ NWs. The W ions were obtained by dissolution of H₂WO₄ in 30% aqueous H₂O₂ followed by dilution in deionized water. As shown in Fig. 3a, while the WO₃ NWs and same-mass W:BiVO₄ film separately generate photocurrents of 1.1 and 0.4 mA/cm² at 1.23 V *vs.* RHE, respectively, the WO₃/W:BiVO₄ NWs generate a photocurrent of 3.1 mA/cm² at 1.23 V *vs.* RHE, which is more than twice the sum of the separate photocurrents, indicating a powerful synergistic effect between the WO₃ core and the W:BiVO₄ shell. This synergy is also evident in the IPCE results (Fig. 3b, measured at 1.23 V *vs.* RHE). As will be described next, light in the 300-515 nm wavelength range is primarily absorbed in the W:BiVO₄ shell, since it is the outer material and a stronger light-absorber than WO₃. Nevertheless, the average IPCE of the WO₃/W:BiVO₄ NWs over the 300-450 nm wavelength range (~60 %) is more than four times higher than that of the

same-mass W:BiVO₄ film (13%), and is similar to the maximum IPCE of the WO₃ NWs. This indicates that the WO₃ NWs are improving the collection efficiency of charges generated in W:BiVO₄, which is a synergistic effect. In other words, these IPCE results suggest that the WO₃/W:BiVO₄ core/shell NWs utilize the best properties of each component in that they absorb light like BiVO₄, and have charge transport properties similar to WO₃, as will be elaborated next.

Next, we determine the reasons for the excellent performance of the WO₃/W:BiVO₄ core/shell NWs by extracting the efficiencies of the sub-processes η_{abs} , η_{sep} , and η_{trans} and comparing them, as appropriate, to those of the bare WO₃ NWs and same-mass W:BiVO₄ film. The wavelength-dependent optical absorption properties of the samples were obtained with an integrating sphere using illumination from a Xe lamp coupled to a monochromator. For the absorption measurements, the samples were placed in the center of the sphere, with light incident normal to the sample surface. For the reflectance measurements, the samples were aligned to a port at the backside of the integrating sphere and the reflectance spectra were normalized to the reflection of a white standard. A calibrated silicon photodiode at a second port was used to measure the unabsorbed and reflected light, respectively. Firstly, the light absorption spectrum of the WO₃/W:BiVO₄ NWs (Fig. 4a) closely resembles that of BiVO₄, with absorption onset at 515 nm (~2.4 eV) and a smooth rise to nearly complete absorption at 450nm. Since the bare WO₃ NWs hardly absorb any light at these wavelengths, the strong light absorption by the core/shell NWs, especially around 450 nm, indicates that light absorption occurs efficiently in the W:BiVO₄ shell despite the small W:BiVO₄ shell thickness of only 60 nm, which is far below the light absorption depth of about 250 nm at 450 nm.^{19, 53} This strong absorption can be attributed to the long path for light, which is equal to the NW length, through the W:BiVO₄ shell. Based on the strong absorption at these longer wavelengths and since it is the outer material, the W:BiVO₄ shell should absorb most of the light in the entire 300-515 nm wavelength range. Nevertheless, some light of wavelength shorter than 460 nm will also enter the WO₃ NW cores through their tips where the W:BiVO₄ coating is very thin, and be absorbed by WO₃. Moreover, η_{abs} of the WO₃/W:BiVO₄ NWs, when the absorption is integrated over the AM 1.5G spectrum, is 69%, which is slightly higher than the 66% η_{abs} of the 1.5 μm -thick porous same-mass W:BiVO₄ film due to reduced reflection by the NWs (Supporting Information Fig. S5). Nevertheless, the light absorption enhancement is much smaller than the over four-fold IPCE enhancement between the WO₃/W:BiVO₄ NWs and same-mass W:BiVO₄ film, indicating that light absorption is not the main reason for the difference in performance of these photoanodes.

The charge separation and surface transfer efficiencies η_{sep} and η_{trans} are determined by adding a fast hole scavenger to the electrolyte.^{4,21} Specifically, J - V curves were measured with 0.5 M H₂O₂ added to the 0.5 M potassium phosphate electrolyte as a hole scavenger. Since the rate of charge transfer to the electrolyte by oxidation of H₂O₂ at the semiconductor/electrolyte interface is very fast, it can be assumed that the surface recombination of charges is eliminated and $\eta_{trans}(H_2O_2) \approx 100\%$.^{13, 19} While the H₂O oxidation photocurrent is given by $J_{H_2O} = J_{max} \times \eta_{abs} \times \eta_{sep} \times \eta_{trans}$, the H₂O₂ oxidation photocurrent is given by $J_{H_2O_2} \approx J_{max} \times \eta_{abs} \times \eta_{sep}$. Since the addition of H₂O₂ did not change the light absorption, pH or flat band potentials of the photoanodes, and the saturated photocurrents for H₂O and H₂O₂ oxidation were the same for

each electrode, indicating that no current doubling occurs in the presence of H₂O₂, J_{max} , η_{abs} and η_{sep} are the same for $J_{H_2O_2}$ and J_{H_2O} .^{13, 19} As shown in Fig. 4b, when H₂O₂ is added to the electrolyte, the WO₃/W:BiVO₄ NWs generate a photocurrent nearly equal to 4.0 mA/cm² at 1.23 V vs. RHE under precisely simulated AM 1.5G illumination, indicating that the $\eta_{abs} \times \eta_{sep}$ ($=J_{H_2O_2}/J_{max}$) product equals 53%, which is the highest value for any reported BiVO₄-based photoanode. The photocurrent onset at around 0.45 V vs. RHE is close to the flat band potential of WO₃ (~0.4 V vs. RHE⁴¹), as expected. Importantly, these high photocurrents at potentials below 1.23 V vs. RHE could be achieved for H₂O oxidation by the addition of OER catalysts. Such a photoanode would then be extremely promising for PEC water-splitting with a tandem photocathode which would supply the necessary bias and perform H₂O reduction.

Moreover, the charge separation and surface transfer efficiencies can be individually calculated as $\eta_{sep} \approx J_{H_2O_2}/(J_{max} \times \eta_{abs})$ and $\eta_{trans} \approx J_{H_2O}/J_{H_2O_2}$, and are plotted in Fig 4c and 4d, respectively. The η_{trans} of the WO₃/W:BiVO₄ NWs (78%) is higher than that of the porous same-mass W:BiVO₄ film (62%) at 1.23 V vs. RHE, perhaps indicating that the surface area of the NWs is higher than that of the porous film. However, this is not sufficient to explain the nearly 8 times higher photocurrent of the WO₃/W:BiVO₄ NWs at 1.23 V vs. RHE, which means that the improvement must primarily come from increased η_{sep} . As expected, charge separation in the same-mass 1.5 μ m-thick polycrystalline W:BiVO₄ (13% at 1.23 V vs. RHE) is extremely poor due to strong bulk recombination, since the average particle radius of 250 nm is larger than the hole diffusion length in W:BiVO₄ (70-100nm^{19, 54, 55}) and the film thickness is much larger than the 300-nm electron diffusion length.⁶ On the other hand, charge separation in the WO₃/W:BiVO₄ NWs (77% at 1.23 V vs. RHE) is relatively more efficient.

Next, we examine the reasons for the high charge separation efficiency of the WO₃/W:BiVO₄ core/shell NWs. Charges are generated mostly by light absorption in the W:BiVO₄ shell, and to a smaller extent by light absorption in the WO₃ NW cores. First, considering charges generated in the 60-nm thick W:BiVO₄ shell, holes can readily reach the semiconductor/electrolyte interface because they only need to travel a short distance that is less than the reported hole diffusion length (70-100nm^{19, 54, 55}) in W-doped BiVO₄. Holes generated in the W:BiVO₄ shell also have a low probability of reaching and recombining at defect states at the FTO/semiconductor interface^{25, 37} because WO₃, due to its lower-lying valence band, serves as a ‘hole mirror’. For electrons, their diffusion lengths in W:BiVO₄ and WO₃ are ~300⁶ and ~500nm,⁵⁶ respectively, which are shorter than the length of the NWs, so the electron transport to the current collector will rely on drift and hence prefer the high electrical conductivity pathway. The axial electron conductivity of the WO₃ NWs (I - V curve and experimental details in Supporting Information Fig. S6) is determined to be on the order of 1 S/cm, which is much higher than that of the 7%-W:BiVO₄ film (10⁻⁸ S/cm) estimated by an impedance measurement (Nyquist plot and experimental details in Supporting Information Fig. S7). Hence, electrons generated in the W:BiVO₄ shell will first travel radially inwards to the WO₃ cores, and then travel to the current collector through WO₃. In addition, apart from the small thickness of the W:BiVO₄ shell, the electric fields due to the gradient W-doping¹⁸ and the staggered type-II WO₃/W:BiVO₄ heterojunction^{41, 46} also significantly improve η_{sep} as evidenced by the fact that

η_{sep} in an undoped BiVO₄ layer of similar thickness was reported to be only 20% at 1.23 V vs. RHE.²⁵ Second, as seen by comparing to η_{sep} of the bare WO₃ NWs (Fig. 4c), charges generated in the 75-nm diameter WO₃ NW cores also have high η_{sep} . Holes can readily reach the electrolyte by first transferring to W:BiVO₄ across the WO₃/W:BiVO₄ heterojunction since the NW diameter is smaller than the hole diffusion length of ~150 nm.⁵⁷ Electrons can reach the current collector directly and efficiently because of the high electrical conductivity of WO₃. Therefore, as a result of efficient charge separation in both the core and shell, the charge separation efficiency in the WO₃/W:BiVO₄ core/shell NWs is much higher than that in the same-mass W:BiVO₄ film.

Compared to the recent top-performer, a 200-nm thick gradient-doped compact W:BiVO₄ film synthesized on a textured substrate which achieved $\eta_{abs} \approx 75\%$ and $\eta_{sep} \approx 60\%$ at 1.23 V vs. RHE,¹⁸ the η_{abs} of the present WO₃/W:BiVO₄ NWs (69%) is very similar despite the small BiVO₄ thickness of 60 nm due to the long optical path for light absorption along the NW length. At the same time, η_{sep} of the present WO₃/W:BiVO₄ NWs (77%) is significantly higher due to the small BiVO₄ thickness (60 nm vs. 200 nm), and the presence of the conductive WO₃ NW pathway for electron transport. The efficiency of the present WO₃/W:BiVO₄ NW photoanodes is also higher than that of a previously-reported WO₃/BiVO₄ core/shell nanorod photoanode⁴⁶ and a WO₃ NW/BiVO₄ heterojunction photoanode,⁴⁷ for a number of reasons. In the case of the previously reported WO₃/BiVO₄ core/shell nanorods,⁴⁶ a thin BiVO₄ layer was deposited onto short (500-1000 nm) WO₃ nanorods which had a hexagonal crystal structure. In the present study, we synthesize longer (2.5 μm) WO₃ NWs with a higher surface area, which permits a higher BiVO₄ loading and therefore higher light absorption, and with a monoclinic WO₃ crystal structure which results in faster electron transport compared to the hexagonal structure, therefore allowing more efficient charge separation. In the case of the previously reported WO₃ NW/BiVO₄ heterojunction, which achieved a photocurrent density of ~2.5 mA/cm² at 1.23 V vs. RHE under simulated AM 1.5G illumination when coated with an OER catalyst and ~2.1 mA/cm² without the OER catalyst,⁴⁷ a 1 μm -thick layer of porous BiVO₄ was deposited on top of a 1 μm -thick porous WO₃ film which was composed of multiple layers of urchin-like structures consisting of short (< 600 nm length) WO₃ NWs. The charge separation efficiency in the present WO₃/W:BiVO₄ NWs is expected to be much higher than in this heterojunction film because of the much smaller BiVO₄ thickness and the presence of continuous WO₃ NW crystals (rather than multiple layers of shorter NWs) which directly conduct electrons to the substrate.

Lastly, the stability of the WO₃/W:BiVO₄ core/shell NWs and their faradaic efficiency for water oxidation were evaluated in a three-electrode configuration with the photoanode (~1 cm² masked area) as the working electrode, a Ag/AgCl (1M KCl) reference electrode, and a Pt wire as the counter electrode. The potential of the photoanode was determined using $V \text{ vs. RHE (volt)} = V \text{ vs. Ag/AgCl (volt)} + [0.059 \text{ (volt)} \times \text{pH}] + 0.236 \text{ (volt)}$. The experiment was conducted in a sealed cell containing 0.5 M Na₂SO₄ electrolyte (pH~ 6) through which He carrier gas was flowed at a rate of 5 sccm. After purging the electrolyte of dissolved oxygen, the potential of the photoanode was held at 1.23 V vs. RHE under simulated AM 1.5G illumination using a potentiostat, and both the photocurrent and the oxygen gas concentration in the He carrier

were monitored (Fig. 5). The concentration of oxygen in the He carrier, as measured by gas chromatography (SRI Instruments), increased and then reached a steady value at around 30 minutes once the dissolved oxygen content in the electrolyte reached a steady value. Bubbles were continuously evolved from the photoanode, and the accumulation and release of these bubbles led to the observed variations in photocurrent over the duration of the measurement. The photocurrent of the $\text{WO}_3/\text{W}:\text{BiVO}_4$ NWs remained at approximately $3.1 \text{ mA}/\text{cm}^2$ over 1 hour without degradation, and the faradaic efficiency for water oxidation to O_2 was found to be 79%. This result shows that the $\text{WO}_3/\text{W}:\text{BiVO}_4$ NWs are stable and are indeed oxidizing water into O_2 .

In conclusion, the critical advance in this work is the use of an electrically conductive WO_3 NW array to overcome the intrinsically poor charge transport properties of BiVO_4 without compromising light absorption, thereby achieving η_{abs} of 69% and η_{sep} of 77% at 1.23 V vs. RHE, for a combined $\eta_{abs} \times \eta_{sep}$ product of 53% which, to the best of our knowledge, is the highest achieved to date in any BiVO_4 -based photoanode (compared to the highest 45% previously reported¹⁸). Even without any OER catalysts, these core/shell NWs achieve a photocurrent of $3.1 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE under precisely-simulated AM 1.5G illumination, which is quite close to the photocurrent achieved at the same potential by the best-performing BiVO_4 -based photoanode with OER catalysts. If the surface charge transfer efficiency of these core/shell NWs could be improved from 79% to 100% by adding OER catalysts, they would achieve a photocurrent of nearly $4.0 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE. Importantly, the $\text{WO}_3/\text{W}:\text{BiVO}_4$ NWs were synthesized from economical precursors in an inexpensive and scalable manner. These promising results bring us a step closer to efficient photoanodes for tandem PEC water-splitting systems.

ASSOCIATED CONTENT

Supporting Information. Additional SEM images, histograms of nanowire dimensions, more detailed X-ray diffraction data, illumination spectra, reflectance spectra, and raw data from which conductivities were extracted. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

‡These authors contributed equally. Pratap M. Rao and Lili Cai carried out the photoanode synthesis and characterization. Pratap M. Rao, Lili Cai and Xiaolin Zheng conceived the study and wrote the manuscript. Chong Liu measured the stability and faradaic efficiency of the photoanodes and participated in revision of the manuscript. In Sun Cho assisted in preparation of reagents for the synthesis and in the electrochemical characterization, and participated in revision of the manuscript. Chi Hwan Lee performed the single-nanowire conductivity measurements. Jeffrey M. Weisse performed the thin film impedance measurements. All authors have commented on the manuscript.

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COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.

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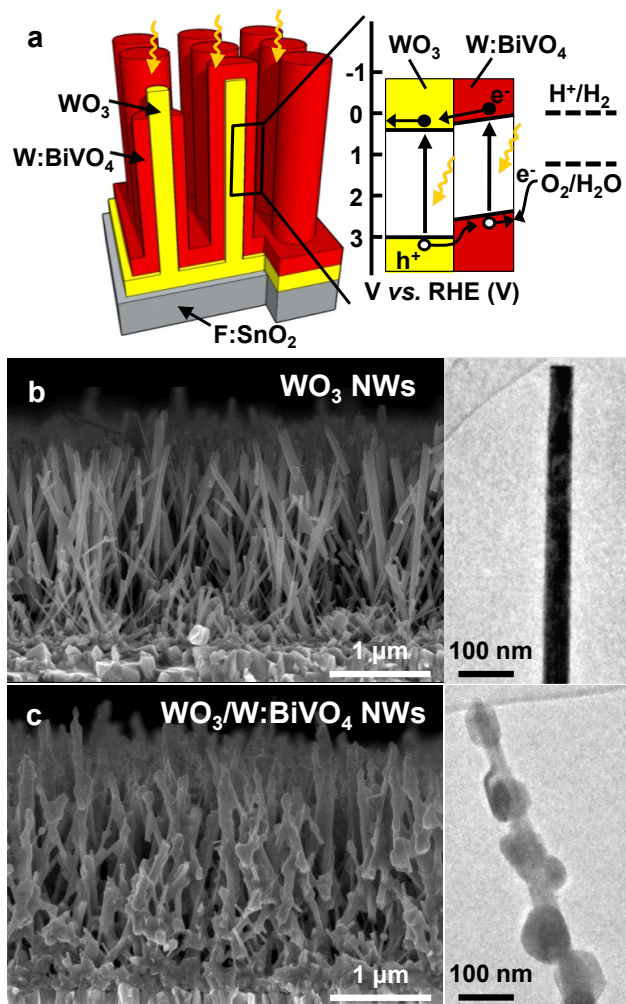


Figure 1. The $\text{WO}_3/\text{W:BiVO}_4$ core/shell nanowire (NW) photoanode. (a) Structural schematic and energy band diagram of the core/shell NWs and type-II staggered heterojunction, in which charges generated in both the W:BiVO_4 shells and WO_3 NW cores can contribute to the water oxidation photocurrent. The band edges and water oxidation and reduction potentials are plotted on the reversible hydrogen electrode (RHE) scale. (b) and (c), Scanning electron microscope (SEM, left) and transmission electron microscope (TEM, right) images of the bare WO_3 NW array (75 nm average NW diameter) and $\text{WO}_3/\text{W:BiVO}_4$ core/shell NWs (60 nm average W:BiVO_4 shell thickness), respectively. The W:BiVO_4 shell consists of a single layer of densely packed nanoparticles.

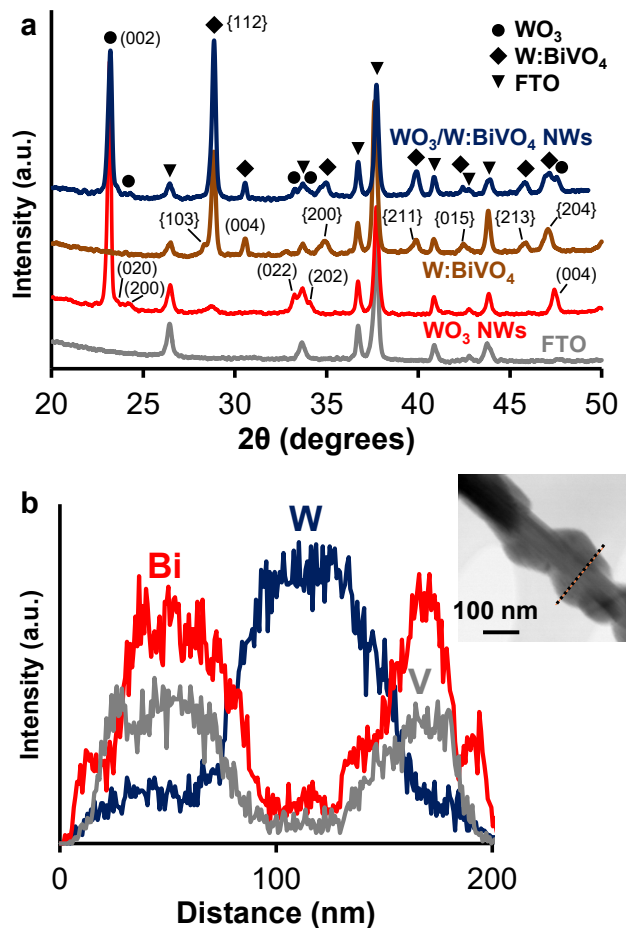


Figure 2. Crystallographic and chemical characterization of the WO₃/W:BiVO₄ core/shell NWs and control samples. (a) X-ray diffraction (XRD) patterns of the WO₃/W:BiVO₄ NWs, a porous planar W:BiVO₄ film containing the same mass of Bi as that in the core-shell NWs (hereafter referred to as the same-mass W:BiVO₄ film), the bare WO₃ NWs, and the bare FTO (fluorine-doped tin oxide) substrate, showing that monoclinic WO₃ and monoclinic W:BiVO₄ are the only phases present in the WO₃/W:BiVO₄ core/shell NWs. The (002) peak of WO₃ is enhanced relative to the (020) and (200) peaks, indicating that the WO₃ NW axis is along the [001] direction of the NW crystals. (b) Results of TEM-energy dispersive X-ray spectroscopy (TEM-EDS) on the WO₃/W:BiVO₄ core/shell NW pictured in the inset TEM image, showing the interdiffusion of elements at the interface and gradient doping of W into the BiVO₄ shell.

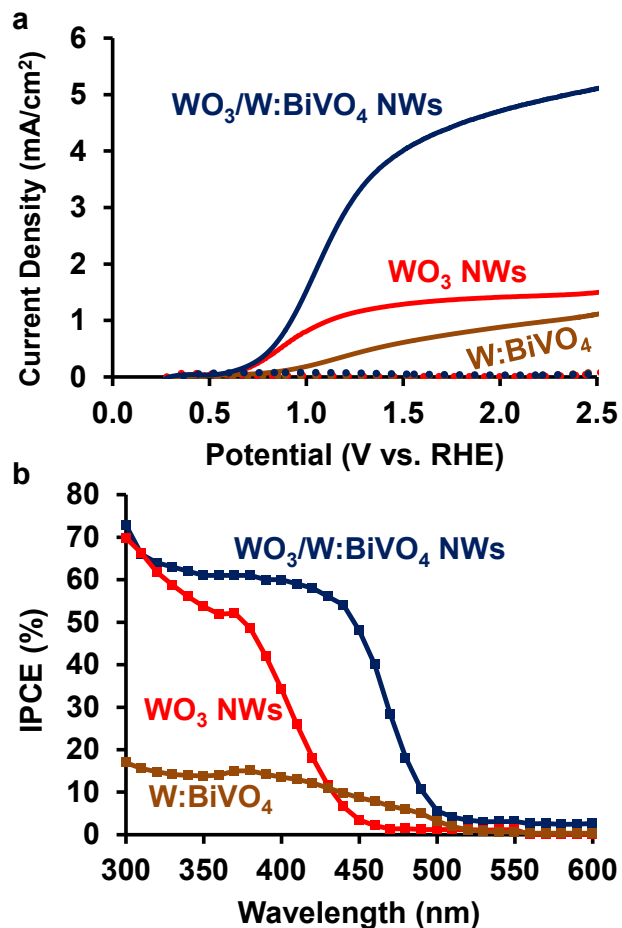


Figure 3. Photoelectrochemical response of the $\text{WO}_3/\text{W:BiVO}_4$ NW photoanode and control samples in 0.5 M potassium phosphate electrolyte buffered to pH 8. (a) Current-voltage ($J-V$) curves (solid lines: simulated AM 1.5G illumination, dotted lines: dark) and (b) Incident photon-to-current efficiency (IPCE) measured at 1.23 V_{RHE} .

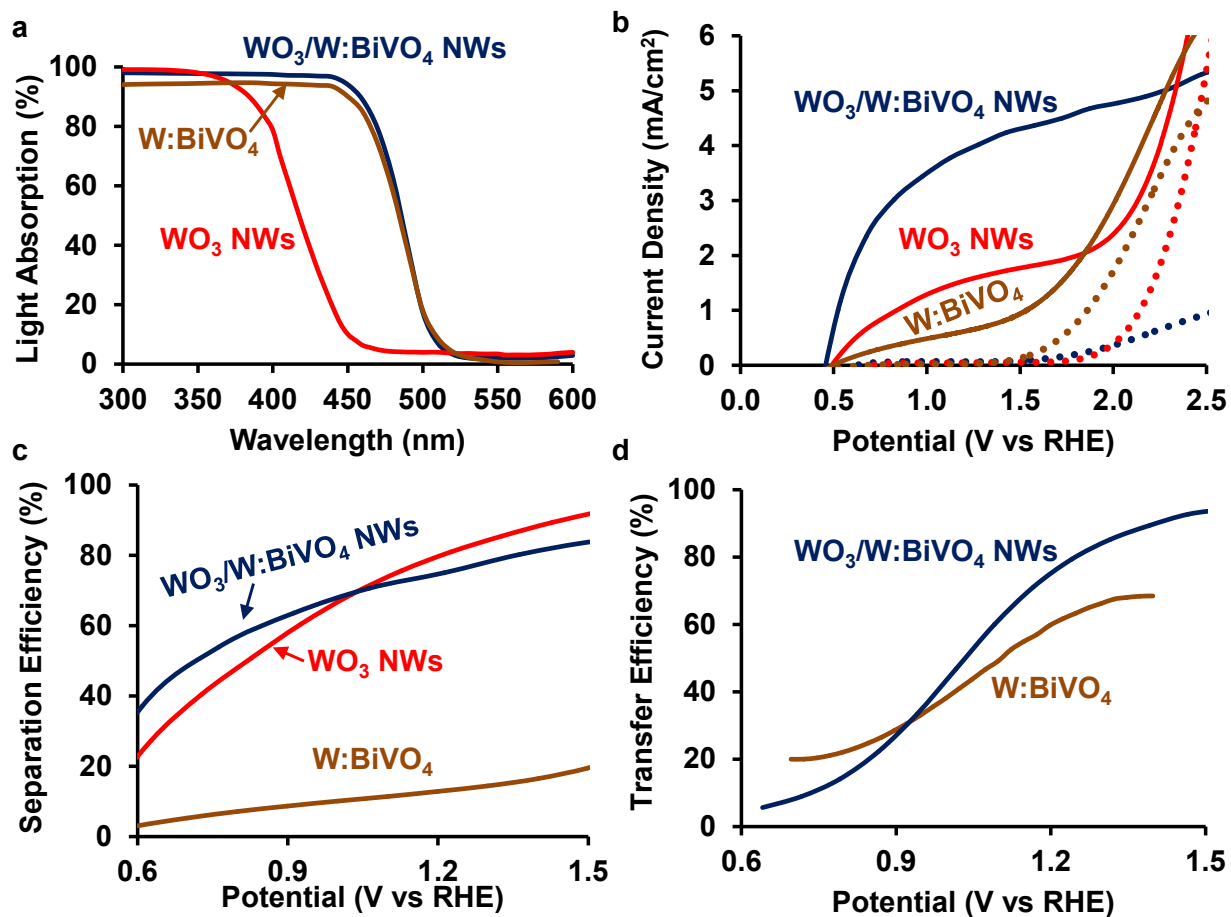


Figure 4. Efficiencies of sub-processes that comprise the overall photoelectrochemical response of the $\text{WO}_3/\text{W:BiVO}_4$ NW photoanode and control samples. (a) Light absorption efficiency (η_{abs}) and (b) J - V curve under simulated AM 1.5G illumination with H_2O_2 added to the potassium phosphate electrolyte as a hole scavenger, which demonstrates the photocurrent achieved when the surface charge transfer efficiency is nearly 100%. (c) Charge separation (η_{sep}) and (d) surface charge transfer efficiency (η_{trans}) of the $\text{WO}_3/\text{W:BiVO}_4$ NWs and, where appropriate, the bare WO_3 NWs and same-mass W:BiVO_4 film.

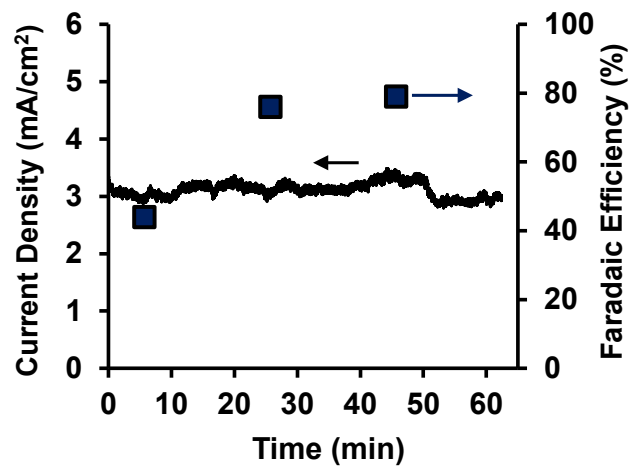


Figure 5. Stability and faradaic efficiency of the $\text{WO}_3/\text{W}:\text{BiVO}_4$ NW photoanode in 0.5 M Na_2SO_4 under simulated AM 1.5G illumination.