Supporting Information for:

Photoanode with enhanced performance achieved by coating $BiVO_4$ onto ZnO-templated Sb-doped SnO_2 nanotube scaffold

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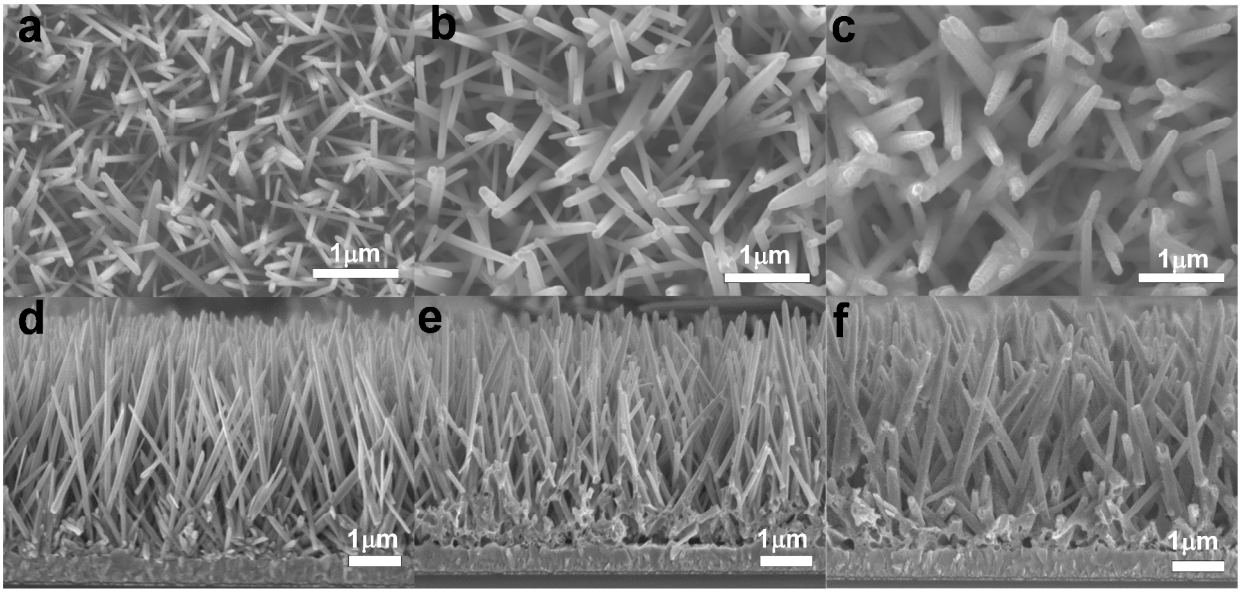


Figure S1. Scanning electron microscopy (SEM) of a) top and d) cross-section of ZnO nanowires, b) top and e) cross-section of Sb:SnO_2 nanotubes, c) top and f) cross-section of Sb:SnO_2/$BiVO_4$ nanotubes photoanode.

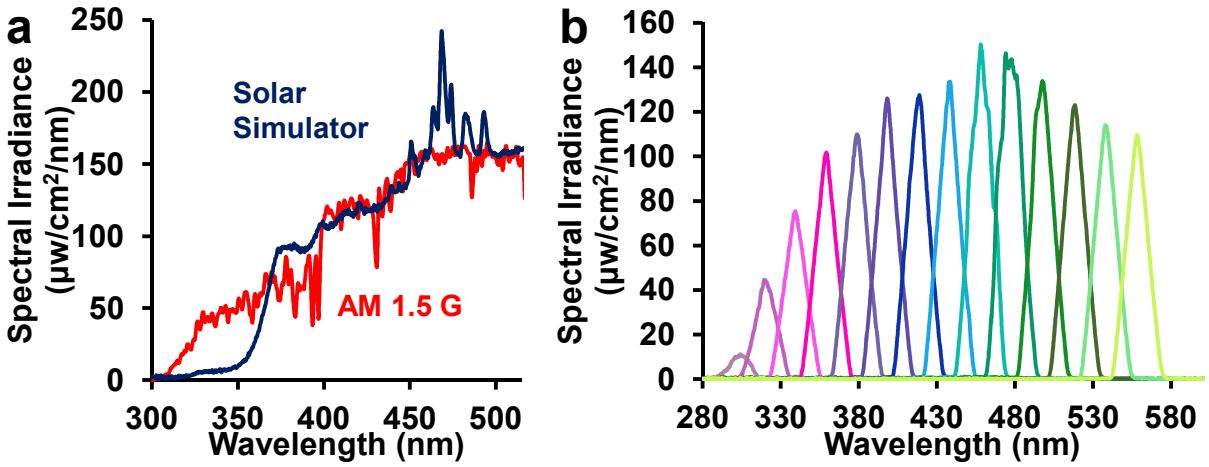


Figure S2. a) Spectral irradiance of Xe lamp solar simulator equipped with AM 1.5 G filter (blue) and standard AM 1.5 G solar spectrum (red). b) Spectral irradiance of incident monochromatic light for IPCE measurements. In both (a) and (b), spectra are recorded after the light has passed through the wall of the glass beaker, in which the photoelectrochemical measurement is conducted.

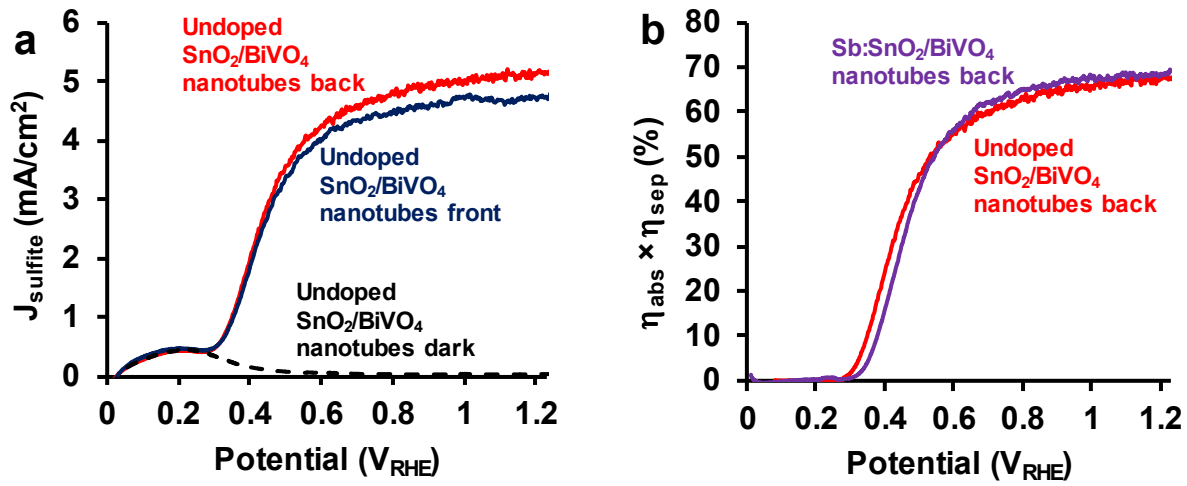
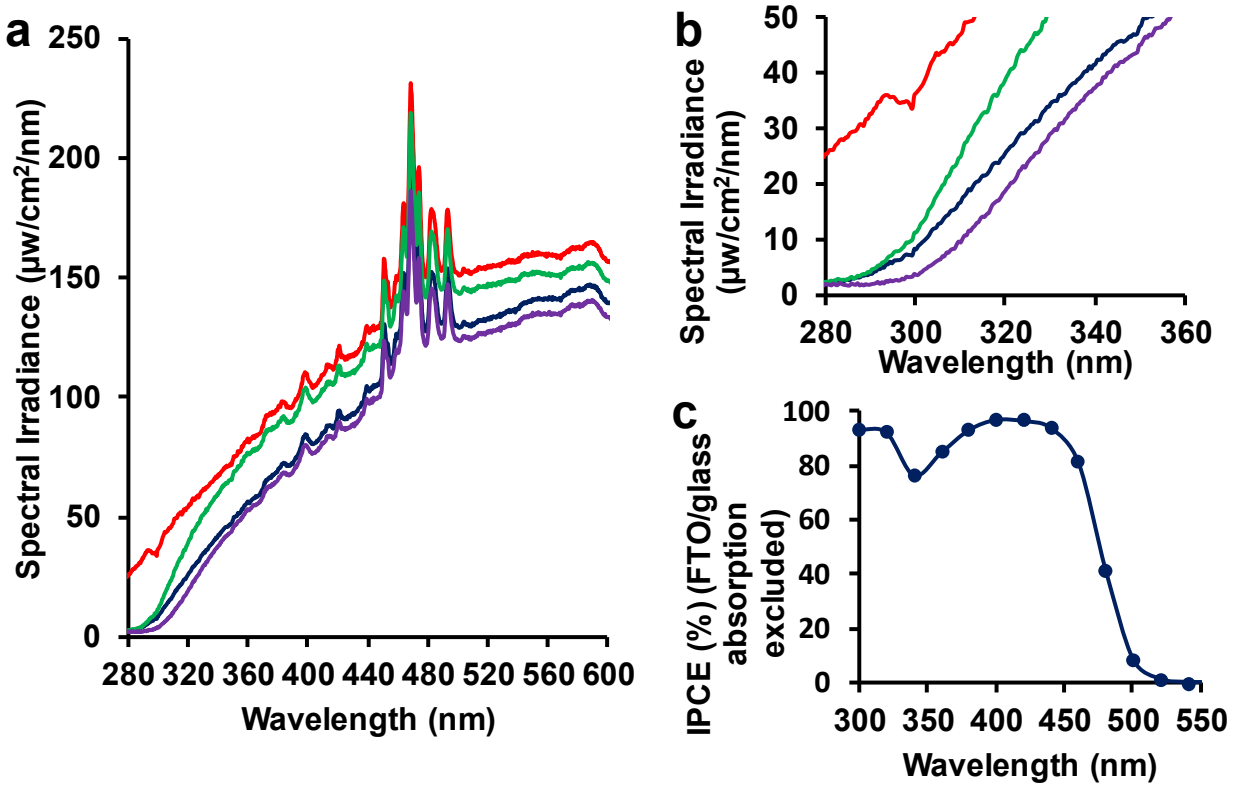


Figure S3. a) Plots of current density ($J_{sulfite}$) versus potential for undoped SnO_2 coated with 4 layers $BiVO_4$ (undoped $SnO_2/BiVO_4$ nanotubes) under front (blue) and back (red) illumination and in the dark (black dashed), measured using a 3-electrode configuration in aqueous phosphate buffer (pH 7) with 1M Na_2SO_3. b) Product of light absorption and charge separation efficiency ($\eta_{abs} \times \eta_{sep}$) versus potential, with dark currents subtracted for undoped $SnO_2/BiVO_4$ nanotubes and Sb:$SnO_2/BiVO_4$ nanotubes.



d	Glass beaker	FTO/ glass	Glass beaker + FTO/glass	(Glass beaker + FTO/glass) / Glass beaker
Transmission percentage (%) at 300nm	33.85	24.55	12.32	36.40

Figure S4. a) and b) spectral irradiance of Xe lamp solar simulator (red), Xe lamp solar simulator passing through the wall of glass beaker (green), Xe lamp solar simulator passing through FTO/glass (blue), Xe lamp solar simulator passing through the wall of glass beaker and FTO/glass (purple). c) Incident photon-to-current efficiency (IPCE) of Sb:SnO_2/$BiVO_4$ under back illumination at 0.6 V_{RHE} with light absorbed in FTO/glass excluded from the calculation of P_{mono}. d) Table of 300 nm wavelength light transmission percentage of glass beaker and FTO.

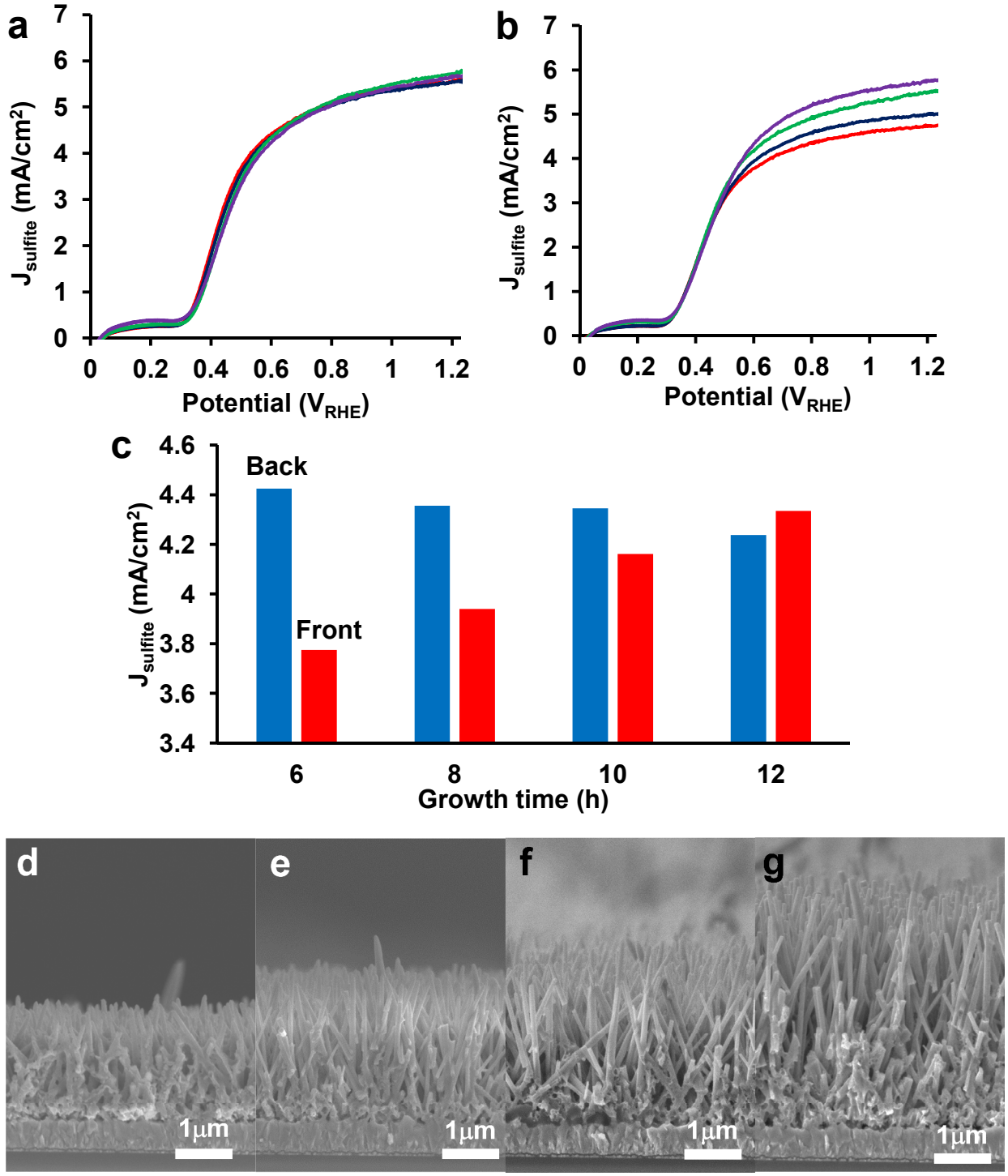


Figure S5. Photoelectrochemical performance and SEM cross-section images of Sb:SnO_2 nanotubes of different lengths (different growth time of ZnO nanowires that were used as templates) coated with the same amount (4 times drop-casting) of $BiVO_4$ to form Sb:SnO_2/$BiVO_4$ nanotubes. Photocurrent for sulfite oxidation ($J_{sulfite}$) measured using a 3-

electrode configuration in aqueous phosphate buffer (pH 7) with 1M Na_2SO_3 under a) back-side and b) front-side simulated AM 1.5G illumination. Sb:SnO_2/$BiVO_4$ nanotubes obtained using ZnO nanowire templates that were grown for 6 h, 8 h, 10 h and 12 h are shown in red, blue, green and purple, respectively. c) Histogram summarizing photocurrent for sulfite oxidation ($J_{sulfite}$) at 0.6 V_{RHE} under front- and back-side illumination. SEM cross-section images of Sb:SnO_2/$BiVO_4$ nanotubes obtained using ZnO nanowire templates that were grown for d) 6 h, e) 8 h, f) 10 h and g) 12 h.

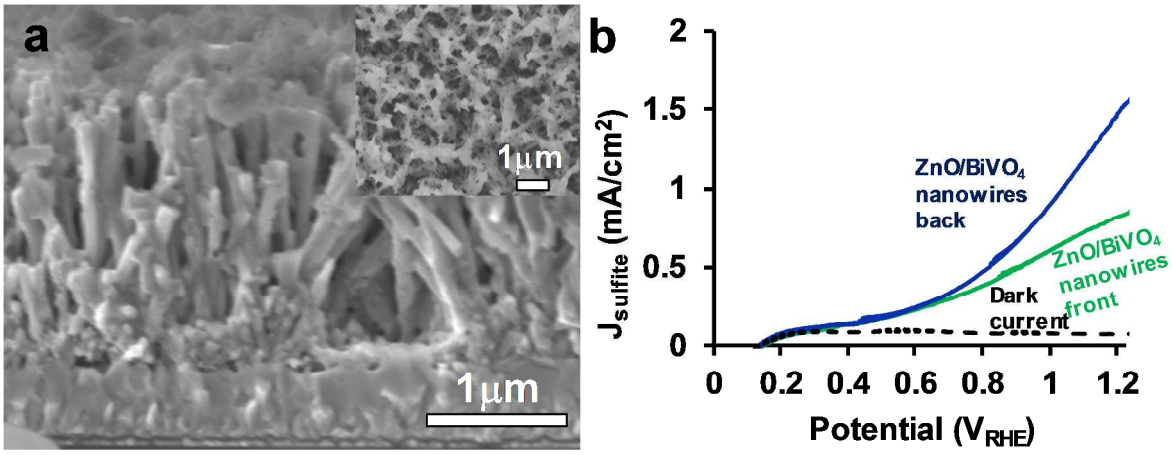


Figure S6. a) SEM images and b) J-V curves of $BiVO_4$ deposited directly onto 6-hr-grown ZnO nanowires using a 2-methoxy ethanol + acetylacetone solvent. Photocurrents are for sulfite oxidation ($J_{sulfite}$) measured under simulated AM 1.5 G illumination using a 3-electrode configuration in aqueous phosphate buffer (pH 7) with 1M Na_2SO_3.

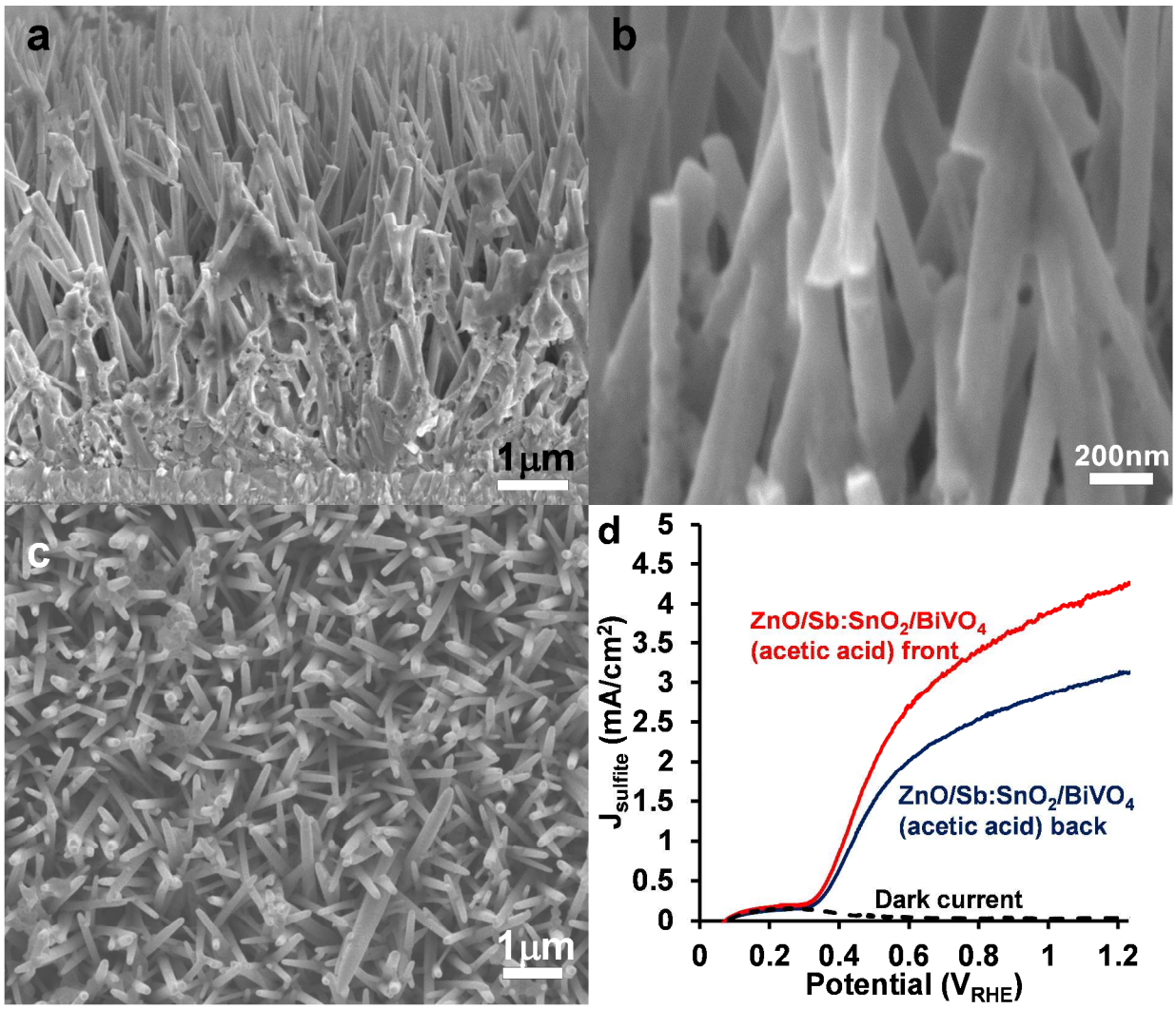


Figure S7. a-c) SEM images and d) J-V curves of $BiVO_4$ deposited onto 12-hr-grown ZnO core/Sb:SnO_2 shell nanowires using an acetic acid + acetylacetone solvent without intentionally etching away the ZnO cores beforehand. Photocurrents are for sulfite oxidation ($J_{sulfite}$) measured under simulated AM 1.5 G illumination using a 3-electrode configuration in aqueous phosphate buffer (pH 7) with 1M Na_2SO_3.

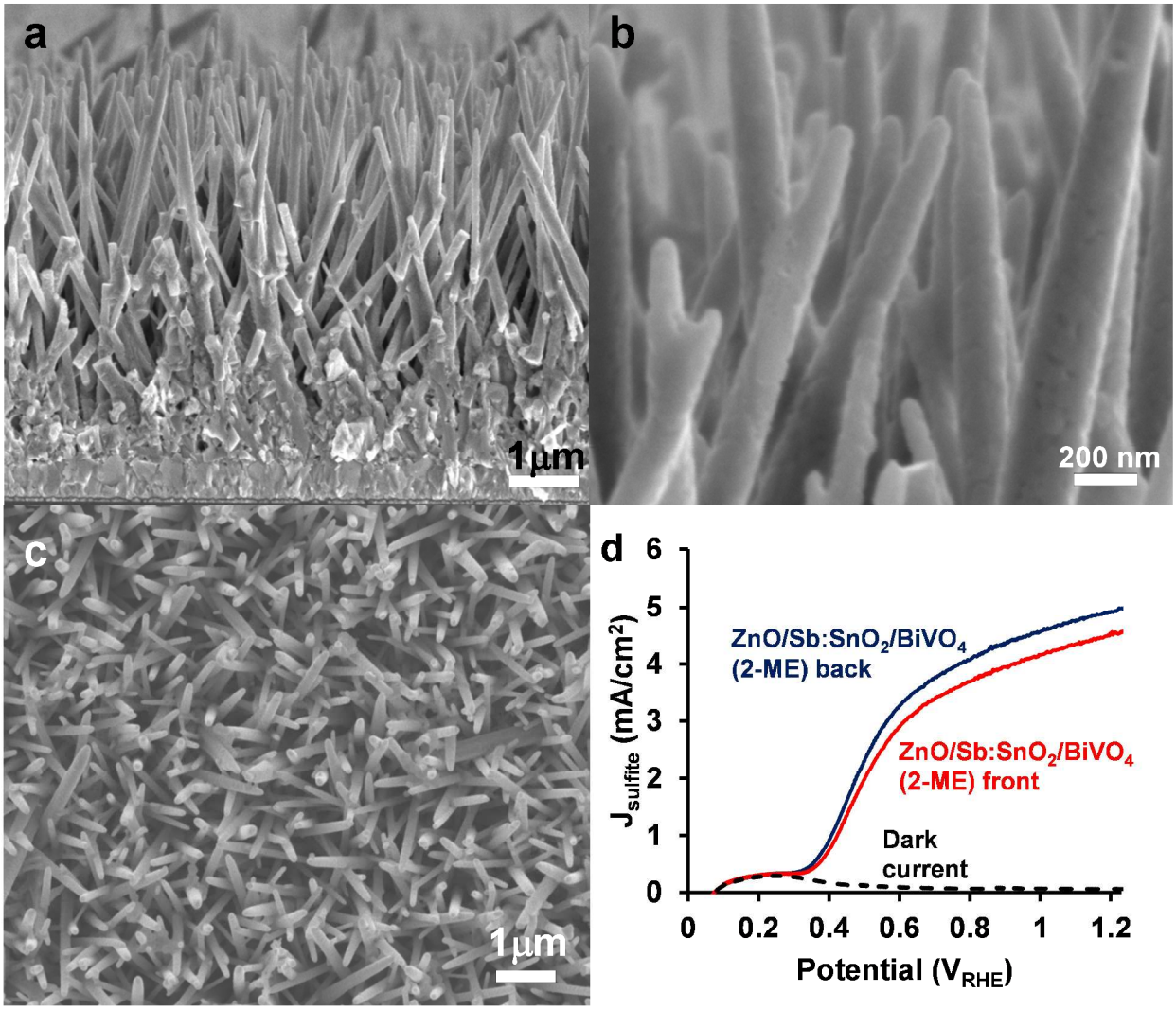


Figure S8. a-c) SEM images and d) J-V curves of $BiVO_4$ deposited onto 12-hr-grown ZnO core/Sb:SnO_2 shell nanowires using a 2-methoxy ethanol + acetylacetone solvent. Photocurrents are for sulfite oxidation ($J_{sulfite}$) measured under simulated AM 1.5 G illumination using a 3-electrode configuration in aqueous phosphate buffer (pH 7) with 1M Na_2SO_3.

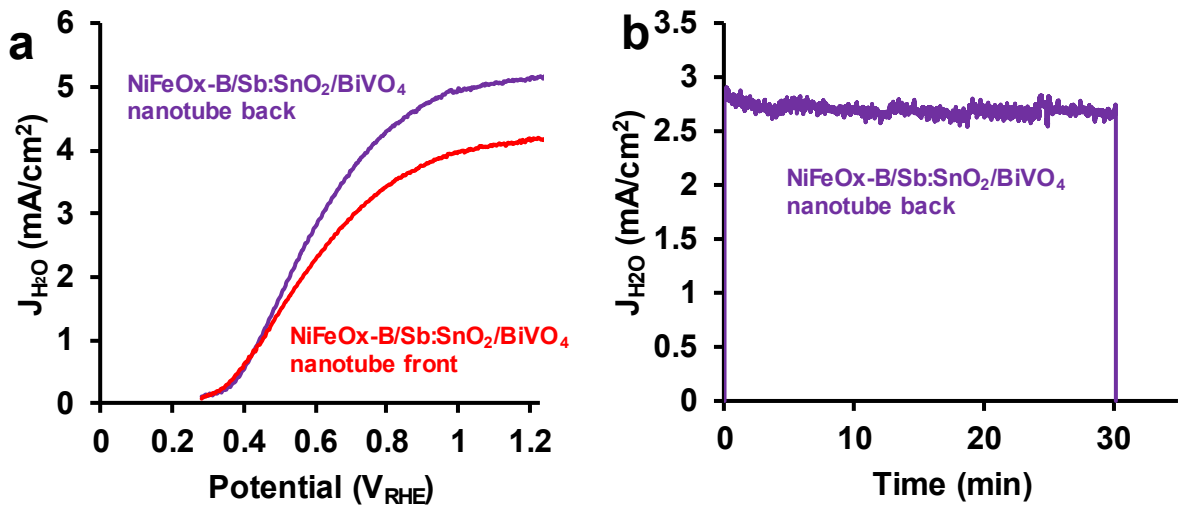


Figure S9. Performance of $Sb:SnO_2/BiVO_4/NiFeOx$-B for photoelectrochemical water oxidation, measured using a 3-electrode configuration in aqueous 1M potassium borate (pH 9) solution (a) Plots of current density (J_{H2O}) versus potential (V_{RHE}) for $Sb:SnO_2/BiVO_4/NiFeO_x$-B nanotubes under front illumination (red) and under back illumination (purple) (b) Stability test of $Sb:SnO_2/BiVO_4/NiFeO_x$-B nanotubes at $0.6V_{RHE}$ under back illumination.

EXPERIMENTAL METHODS

Synthesis procedures for $Sb:SnO_2/BiVO_4$ nanotube photoanodes:

Firstly, hydrothermal growth of ZnO nanowire templates was adapted from several previous reports.[1, 2] Arrays of ZnO nanowires were synthesized on 2 cm * 2.5 cm FTO substrates (Hartford Glass, IN), that were first cleaned thoroughly by acetone + isopropyl alcohol + deionized water with sonication, and then coated with seed layer (5 mM zinc acetate dihydrate in ethanol) by spin coating at 2000 rpm for 30 s. Samples with seed layer were annealed at 350°C for 0.5 hour.

ZnO nanowires were grown by immersing seeded substrates in aqueous solution containing 25 mM zinc nitrate hexahydrate (98%, Sigma Aldrich), 25mM hexamethylenetetramine (99%, Sigma Aldrich) and 5-7 mM polyethylenimine (branched, Aldrich) at 90-95°C for 2 hours. After first time growth of 2 hours, substrates were repeatedly introduced to fresh solution (20 mM zinc nitrate hydrate, 20mM hexamethylenetetramine and 5-6 mM polyethylenimine) for 2 hours at a time in order to obtain long nanowire arrays. The total reaction time was 6 hours, 8 hours, 10 hours or 12 hours. The arrays were then rinsed with deionized water and annealed in air at 400°C for 0.5 hours to remove any residual organics.

The $Sb:SnO_2$ nanotube arrays were synthesized by coating $Sb:SnO_2$ layers onto the ZnO nanowire templates. $Sb:SnO_2$ solution containing 0.1225g $SnCl_2$ (98%, Sigma Aldrich) and 0.01g $SbCl_3$ (99%, Sigma Aldrich) in 10 mL 2-methoxyethanol (99%, Alfa Aesar) was firstly spin coated on the ZnO nanowire templates. After 5 layers of $Sb:SnO_2$ coating, the substrates were annealed in air at 550^{o}C for 2 hours to crystallize the $Sb:SnO_2$ nanotube shell. Then, the ZnO nanowire templates with the $Sb:SnO_2$ shell was etched in acetic acid (99.7%, Sigma Aldrich) for 4 hours and thoroughly washed in DI water to remove all the ZnO. The samples were then again spin coated with 5 more layers of $Sb:SnO_2$ solution, annealed and etched in acetic acid one more time to make the $Sb:SnO_2$ nanotube walls thicker and further decrease the possibility of Zn doping in the outer layers of the $Sb:SnO_2$ nanotubes, which might otherwise dope into the $BiVO_4$ shell.

The $BiVO_4$ drop casting method was based on our previous report. The $Sb:SnO_2$ nanotube arrays on the substrate were soaked in acetic acid for 10mins and then dried by air-gun

to improve the subsequent wetting and coating of the nanotube arrays by the drop-casting solution. One edge of the substrate was then covered with Scotch tape measuring 1 x 0.85 cm (to preserve an uncoated area that was later used to make electrical contact to the FTO/Sb:SnO_2 nanotube arrays current-collector), leaving an area of 1 cm × 1.15 cm to be coated with $BiVO_4$. 2 drops of 5 μL solution were then dropped onto the Sb:SnO_2 nanotube arrays, which was then dried on a hotplate set at 500^oC in air for 10 minutes to make one $BiVO_4$ drop-casted layer. After 4 layers of drop-casting, the sample was annealed in a furnace in air at 550^oC for 2 hours to crystallize the $BiVO_4$ and form the core/shell Sb:SnO_2/$BiVO_4$ nanotubes photoanode. To prepare the photoanode for PEC measurements, an electrical connection was then made to the exposed FTO/Sb:SnO_2 nanotube arrays part of the photoanode by bonding a nickel wire using silver epoxy (Circuit Works No. 16043). The silver epoxy, any exposed FTO/Sb:SnO_2 NRA substrate area, and the portion of the nickel wire that would be submerged in the electrolyte were then all covered thoroughly with non-conductive epoxy (Loctite 1C Hysol). Optical images of ZnO nanowires, Sb:SnO_2 nanotubes and Sb:SnO_2/$BiVO_4$ nanotubes photoanode are provided in Figure S10.

Procedures for photoelectrochemical measurements:

The PEC performance of the Sb:SnO_2/$BiVO_4$ nanotubes was evaluated by measuring the current density-voltage (J-V) curve (i.e. linear sweep voltammogram) and wavelength-dependent incident photon-to-current efficiency (IPCE) under both front-side (electrolyte-side) and back-side (glass-side) illumination in a three-electrode configuration using a potentiostat (Model SP-200, BioLogic), with the photoanode as working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt wire as the counter electrode. The entire exposed area of the photoanode (1.14cm^2) was used in all calculations of photocurrent density. The J-V curve was measured at a scan rate of 25 mV/s and the IPCE was measured at a voltage of 0.6 V_{RHE}, and both measurements were made in 0.5 M potassium phosphate aqueous solution buffered to pH 7 with 1M sodium sulfite (Na_2SO_3) added as a hole scavenger. For J-V measurements, the simulated solar illumination was provided by a Xe lamp (Model 6258, Oriel) equipped with an AM 1.5G filter (Model 81094, Oriel). For IPCE measurements, the illumination was provided by a Xe lamp (Model 6258, Oriel) equipped with a monochromator (Cornerstone 130 1/8 m, Newport). The spectral irradiance in both J-V and IPCE measurements was measured inside a

glass beaker (filtered by the wall of the glass beaker) by a spectrometer (Model USB2000+Rad, Ocean Optics). The transmission spectrum of glass beaker and FTO/glass substrate are plotted in Figure S4.

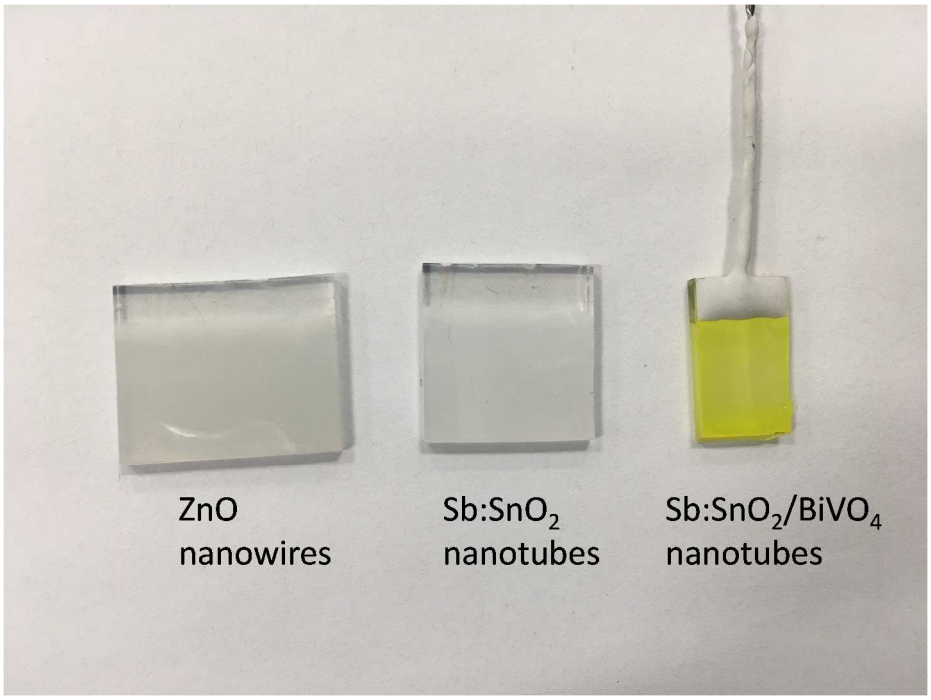


Figure S10. Optical image of ZnO nanowires (left), $Sb:SnO_2$ nanotubes (middle), $Sb:SnO_2/BiVO_4$ nanotubes (right).

References

(1) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. Nanowire dye-sensitized solar cells. *Nat. Mater.* **2005,** *4*, 455-459.

(2) Greene, L. E.; Law, M.; Tan, D. H.; Montano, M.; Goldberger, J.; Somorjai, G.; Yang, P. General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds. *Nano Lett.* **2005,** *5*, 1231-1236.