New Electrochemical Synthesis Route for a BiOI Electrode and Its Conversion to a Highly Efficient Porous $BiVO_4$ Photoanode for Solar Water Oxidation

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Supporting Information

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Experimental Section

Electrochemical synthesis of BiOI electrodes: A standard three-electrode set-up in an undivided cell was used for all depositions. Fluorine-doped tin oxide (FTO) (sheet resistance ~8-12 Ω, Hartford Glass Company) was used as the working electrode (WE) while a platinum electrode, which was prepared by sputter coating 200 Å Ti layer followed by 1000 Å Pt layer on cleaned glass substrates, was used as the counter electrode. The reference electrode was an Ag/AgCl electrode in 4 M KCl solution, against which all the potentials reported herein were measured. A PAR VMP2 Potentiostat was used for electrodeposition and all subsequent electrochemical studies. The plating solution was prepared by dissolving 40 mM $Bi(NO_3)_3$ (Sigma Aldrich, ≥98.0%) in a 400 mM KI (Acros, 99+%) aqueous solution. The pH of the resulting opaque orange solution was adjusted to 1.75 using dilute HNO_3 (Mallinckrodt, 68.0-70.0%), which converts the opaque solution to a transparent red-orange solution. 50 mM p-benzoquinone (Sigma Aldrich 98%) was then added to the solution, resulting in a dark transparent black solution with a pH of 2.6. The depositions were carried out potentiostatically at -0.1 V for 10 min at room temperature (average current density -0.27 mA/cm^2). After the deposition, the electrode was rinsed with deionized water and dried with a gentle stream of nitrogen gas. Upon this layer, a second round of BiOI deposition was carried out at a higher temperature, 75 °C, in order to increase the coverage of the WE by BiOI. The plating solution was prepared by first heating a solution of 400 mM KI to 75 °C then adding 20 mM $Bi(NO_3)_3$. The pH of the resulting opaque orange solution was adjusted to 1.75 using dilute HNO_3 converting the opaque solution to a transparent red-orange solution. The solution was then reheated to 75 °C and 50 mM p-benzoquinone was added changing the pH to 2.6. The deposition was carried out potentiostatically on top of the existing BiOI film at -0.1 V for 10 min at 75 °C (average current density, -1.67 mA/cm^2). After deposition, the electrode was rinsed with deionized water and dried with a gentle stream of nitrogen gas.

Thermal Conversion to $BiVO_4$: $BiVO_4$ electrodes were prepared by pipetting 75 μL NH_4OH (Macron 28.0-30.0%) solutions of 100 mM V_2O_5 (Sigma Aldrich ≥98.0%) onto a 1 cm x 1.5 cm x *ca.* 2 μm BiOI layer to completely cover the BiOI crystals. The resulting wet electrode was transferred to a furnace and annealed in air at 520 ˚C for 6 h after a ramp rate of 2 °C/min. The annealing procedure resulted in decomposition of BiOI into Bi_2O_3 and I_2. After the solution evaporated and I_2 sublimed, only the remaining Bi_2O_3 and V_2O_5 reacted to form $BiVO_4$. Annealing times shorter than 6 h resulted in Bi_2O_3 impurities while annealing longer did not improve crystallinity. After the heat treatment, the electrode was soaked in 1 M NaOH (Macron, pellets) solution for 20 min while stirring to remove excess V_2O_5 that did not react to form $BiVO_4$.

Deposition of FeOOH: A layer of FeO(OH) was photodeposited onto the surface of $BiVO_4$ in a 0.1 M $FeCl_2$ (Alfa Aesar, 99%) solution (pH 4.1) while stirring. A standard three-electrode set-up in an undivided cell was used using the counter and reference electrodes mentioned above. $BiVO_4$ films were used as the working electrode. Illumination was provided using a 300 W ozone-free xenon lamp after passing through water, neutral density, and AM 1.5G filters. The intensity of the light that hit the $BiVO_4$ surface was 1.6 mW/cm^2. The $BiVO_4$ electrode was illuminated through the FTO substrate (back illumination). An external bias of +0.27 V was applied to the WE during photodeposition to increase the photodeposition current, which decreased the optimum deposition time to 1 hr. After photodeposition, additional electrodeposition of FeOOH was carried out using the same $FeCl_2$ solution by applying +1.2 V for 10 min in the dark in order to deposit on FeOOH on any bare FTO substrate exposed between $BiVO_4$ particles.

Characterization: Surface morphology of the electrodes was examined using a field emission scanning electron microscope (FEI Nova NanoSEM) operated at 10 kV with a working distance of approximately 5 mm. The electrodes were coated with Pt using a thermal evaporator before imaging to minimize charging problems. Samples were prepared for energy dispersive spectroscopy (EDS) by scraping films off FTO substrates and piling onto carbon tape. Since our films are thinner than the penetration depth of the X-rays used for EDS analysis, this procedure ensures that the majority of the EDS signals is generated by the sample and not by the substrate, which improves the accuracy of the results. EDS analysis was completed using an Oxford Inca system coupled to the FEI Nova NanoSEM. X-ray diffraction patterns were obtained using a Bruker D8 Focus (Cu K_α radiation). UV-Vis spectra of the films were measured using a Cary 300 UV-Vis spectrophotometer in dual-beam transmittance mode with bare FTO substrate as a reference.

Electrochemical and Photoelectrochemical Measurements: Photoelectrochemical measurements were taken with a PAR VMP2 Potentiostat using a three-electrode configuration with the sample as the working electrode, an oversized platinum (1000 Å sputtered on glass, 200 Å Ti adhesion layer) as a counter electrode, and a Ag/AgCl (4 M KCl) reference electrode, against which all further measurements mentioned herein will be referenced. Illumination was provided by a 300 W ozone-free xenon lamp after passing through neutral density filters, a water filter, and an AM 1.5G filter into an optical fiber and calibrating the output to 100 mW/cm^2 using a thermopile detector from International Light. The illuminated area of the samples was either 0.1 or 0.2 cm^2 for all measurements. All samples were back-illuminated through the FTO glass because back-illumination resulted in a much higher photocurrent generation. All experiments were performed in a 0.1 M potassium phosphate solution (KH_2PO_4, Alfa Aesar, ACS grade) with pH adjusted to 7 using KOH. In some experiments 0.1 M Na_2SO_3 (Mallinckrodt, ≥98.0%) was added to the electrolyte to compare photocurrents obtained from sulfite oxidation and water oxidation. Before photocurrent measurement, each electrode was fully illuminated until the most negative and stable open circuit potential value was obtained, which could take 10 min to 3 h. Photocurrent measurements were carried out while linearly sweeping potential in the positive direction with a scan rate of 10 mV/s or while applying a constant potential of -0.1 V vs. Ag/AgCl (4 M KCl). While all measurements were carried out using a Ag/AgCl (4 M KCl) reference electrode, results in this study were presented against reversible hydrogen electrode (RHE) for ease of comparison with the H_2 and O_2 redox levels and with other literature reports that used electrolytes with different pH conditions. Potentials were converted using the following equation.

$$E\text{ (vs. RHE)} = E\text{ (vs. Ag/AgCl)} + E_{\mathrm{Ag/AgCl}}\text{ (ref)} + 0.0591\text{ V} \times \mathrm{pH}$$

$$(E_{\mathrm{Ag/AgCl}}\text{ (ref)} = 0.1976\text{ V vs. NHE at 25 °C})$$

Capacitance measurements were carried out to obtain Mott-Schottky plots using an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 263A interlinked with a Princeton Applied Research FRD100 frequency response detector using the PowerSine software program. A sinusoidal modulation of 20 mV was applied at a frequency of 5 kHz or 10 kHz. The solution and the electrode set-up were identical to those used for photocurrent measurement.

Oxygen Detection: Oxygen was detected quantitatively using an Ocean Optics fluorescence-based oxygen sensor (FOSPOR-R 1/16”). The electrochemical cell was a custom-built air-tight two-compartment cell divided by a frit. One side held a Pt counter electrode, while the other side held the working electrode ($BiVO_4$/FeOOH) along with a Ag/AgCl reference electrode. Both sides were filled with 0.1 M phosphate buffer (pH 7) with both the electrolyte and headspace of the sealed cell purged with argon. The electrolyte in the working compartment was 30.0 mL and the headspace volume was 11.75 mL. The needle probe was inserted through a rubber septum for O_2 readings throughout the experiment. The probe was calibrated using 2 points (argon, 0% O_2, and air, 20.9% O_2), with an error of 5 % of the reading. The experiment began with 30 min of baseline O_2 measurement followed by 2 h of illumination (AM 1.5G, 100 mW/cm^2) while applying 0.5 V vs. RHE. The probe measures the O_2 content in the headspace and records as mole %. This was converted to μmol after first adjusting for the O_2 dissolved in solution using Henry's Law. The charge passed during the experiment was also converted from Coulombs to μmols by dividing by 4 F and multiplying by 10^6 (F = 96485 C/mol).

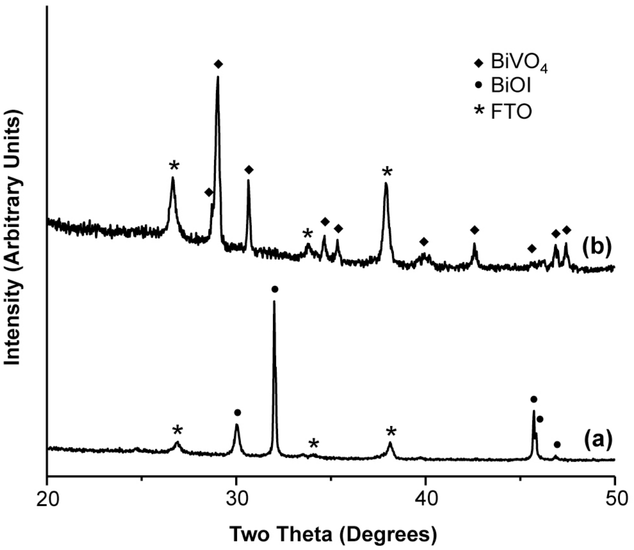

Figure S1. XRD patterns for (a) BiOI and (b) $BiVO_4$.

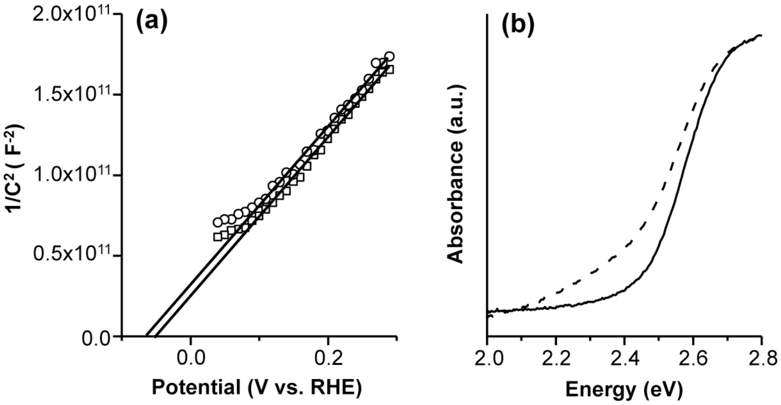

Figure S2. (a) Mott-Schottky plots obtained in 0.1 M phosphate buffer (pH 7) at 5 kHz (□) and 10 kHz (○) of $BiVO_4$ electrodes and (b) UV-vis absorption spectra of $BiVO_4$ (solid) and $BiVO_4$/FeOOH electrodes (dashed).

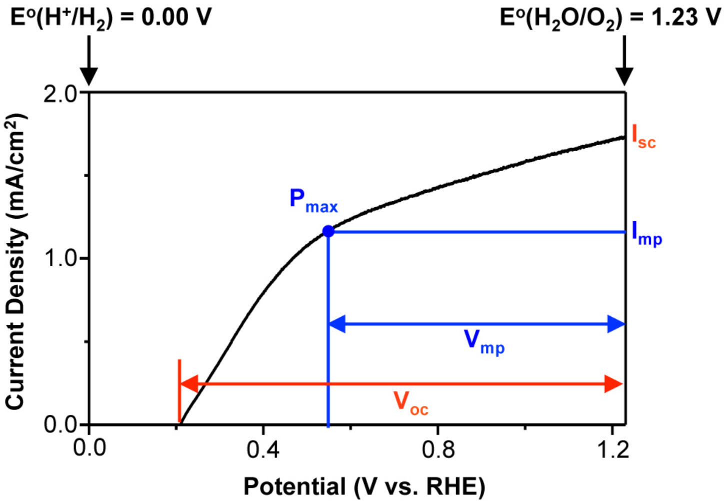

Figure S3. Photocurrent density(J)-voltage(V) characteristics of $BiVO_4$/FeOOH photoanode in 0.1 M phosophate buffer (pH 7) (AM 1.5G, 100 mW/cm^2 illumination) with a scheme showing which points are equivalent to short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) in a J-V curve obtained using a three electrode system for a solar water oxidation half reaction.[21] The current and voltage at maximum power point, P_{max}, is denoted as I_{mp} and V_{mp}, respectively. Then the fill factor can be calculated by (I_{mp} x V_{mp})/(I_{sc} x V_{oc}). Our $BiVO_4$/FeOOH photoanode has V_{oc} = 1.02 V, I_{sc} = 1.72 mA/cm^2, V_{mp} = 0.68 V, I_{mp} = 1.17 mA/cm^2 and fill factor =0.48 for the solar water oxidation half reaction.