Here we report an electrochemical reduction-induced photocurrent enhancement up to an order of magnitude for monoclinic tungsten trioxide (WO3) particulate photoanodes. Electrochemical impedance and photoelectrochemical measurements suggest that the improved performance is attributed to the increase in majority carrier concentration (from \(1.5 \times 10^{18}\) to \(2.5 \times 10^{19}\) cm\(^{-3}\)). This results in higher conductivity and improved electron transport. Minority carrier extraction can be increased by reducing the WO3 particle size from 200 nm to 50 and 30 nm. The larger solid-liquid interface area promotes the water oxidation rate. By balancing electron/hole extraction with photon absorption in an optimized 30 nm WO3 particulate electrode, a record water oxidation photocurrent of 3.8 mA/cm\(^2\), under +1.36 V (vs. RHE) applied bias in 0.1 M Na\(_2\)SO\(_4\) solution at pH = 3.5 is achieved with 50 mW/cm\(^2\) unfiltered Xe illumination.

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Photoelectrochemical water splitting is an efficient way of converting solar energy to chemical fuel by decomposing water into hydrogen and oxygen.\(^{1,9}\) Among inorganic materials that catalyze the photoelectrolysis of water, WO3 with a bandgap of 2.6 eV is attractive due to its visible absorption and its photochemical stability in acid aqueous solution up to pH 5.\(^{10−13}\) Since it was first reported as a potential photoanode for photoelectrochemical cells (PEC) in 1976,\(^{14}\) many aspects of WO3 including synthesis,\(^{15}\) crystal structures,\(^{16}\) as well as its electrochromic phenomena\(^ {16}\) have been extensively studied. Lately efforts have been devoted to promoting minority carrier collection in WO3 through nanostructuring,\(^ {17,18}\) increasing visible absorption via intentional doping,\(^ {22−26}\) improving carrier separation with heterojunctions,\(^ {19−21}\) tailoring photocatalytic selectivity toward water oxidation with electrocatalysts,\(^ {27,28}\) and enhancing WO3 stability in neutral solution using surface coating.\(^ {27}\) Recently, Yat Li’s group reported that a hydrogen treatment at 350 °C increases the water oxidation photocurrent of WO3 by over an order of magnitude for monoclinic WO3 nanoplate films with an average molecular weight of 8000 (PEG 8000) was purchased from Sigma. Potassium sulfate (99% purity) was from Mallinkrodt. Potassium nitrate (99+ % certified ACS grade), potassium chloride (99+ % certified ACS grade), methanol (99.9+ % optima) and sulfuric acid (Certified ACS plus) were purchased from Fisher Scientific. Hydrochloric acid (GR ACS grade) and nitric acid (GR ACS grade) were from EMD Chemicals. SnO\(_2\):F electrodes were purchased from MTI corporation with a SnO\(_2\):F coating layer of <200 nm and a resistivity of 12−14 ohm/sq. Water was purified by Nanopure II system to a resistivity of >17.5 MΩ/cm.

\(\begin{align*}
\text{WO}_3\text{ electrode preparation. — WO}_3\text{ nanoparticles of 500 nm in diameter 50 nm in thickness and nanoparticles of 30 nm diameter were synthesized with and without the addition of PEG 8000 respectively, according to a published procedure by Augustynski.} \quad \text{[15,27]} \\
\text{The precursor solution of tungstic acid was prepared by} \quad \text{[25,26]} \\
\text{passing 5 mL of 0.5 M sodium tungstate (Na}_2\text{WO}_4\text{) aqueous solution through a} \quad \text{[18−21]} \\
\text{proton exchange column packed with 20 mL of protonated Dowex 50 W−X8} \quad \text{[19]} \\
\text{resin. For WO}_3\text{ nanoparticles synthesized with no PEG, the yellow eluate of} \quad \text{[17]} \\
\text{tungstic acid precursor was collected in water and aged with constant} \quad \text{[15]} \\
\text{stirring for one day and used within three weeks to fabricate} \quad \text{[15]} \\
\text{electrodes by dropcasting} \quad \text{[15]} \\
\text{0.2 ml of the precursor solution (equivalent to a concentration of 2.5 mg/ml WO}_3\text{) onto SnO}_2\text{:F substrates at} \quad \text{[15]} \\
\text{100°C. This typically produces WO}_3\text{ nanoplate films with a thickness} \quad \text{[15]} \\
\text{of 2 μm. For WO}_3\text{ nanoparticles synthesized with PEG, the yellow} \quad \text{[15]} \\
\text{eluate of tungstic acid precursor was collected in ethanol and 1.15 g} \quad \text{[15]} \\
\text{of PEG 8000 was added immediately as a stabilizer to control particle} \quad \text{[15]} \\
\text{size and prevent aggregation. The ratio of WO}_3 \quad \text{[15]} \\
to PEG was kept at 0.5 w/w, as suggested.} \quad \text{[15]} \\
The viscous pale yellow precursor solution with PEG 8000 was completely stirred and used within a week to fabricate electrodes by dropcasting 0.2 ml of the precursor ethanol solution (equivalent to a concentration of 2.5 mg/ml WO\(_3\)) onto SnO\(_2\):F substrates at 100°C. The yield WO\(_3\) nanoparticle films are 300 nm in film thickness and composed of particles with 30 nm average diameter. A thicker film of 30 nm WO\(_3\) was also prepared by repetitively applying 0.2 ml of the precursor solution (equivalent to a concentration of 2.5 mg/ml WO\(_3\)) and drying at 100°C until thickness reaches 2 μm. To achieve this, a total amount of 4 mg WO\(_3\) was used. As a comparison, bulk WO\(_3\) particles were also investigated in this study. 600 nm-thick films of bulk WO\(_3\) particles were prepared by sonicating bulk WO\(_3\) powders in water and dropcasting 0.2 ml of 2.5 mg/ml bulk WO\(_3\) suspension onto SnO\(_2\):F substrates at 100°C. All SnO\(_2\):F substrates (1.0 × 2.5 cm\(^2\)) were pre-cleaned by consecutive

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Experimental

**Chemicals.— Sodium tungstate dihydrate Na\(_2\)WO\(_4\)·2H\(_2\)O (99+% ACS purity) and bulk WO\(_3\) (99+% purity) were purchased from Acros Organics and used as received. Polyethylene glycol with an average molecular weight of 8000 (PEG 8000) was purchased from Sigma. Potassium sulfate (99% purity) was from Mallinkrodt. Potassium nitrate (99+% certified ACS grade), potassium chloride (99+% certified ACS grade), methanol (99.9+% optima) and sulfuric acid (Certified ACS plus) were purchased from Fisher Scientific. Hydrochloric acid (GR ACS grade) and nitric acid (GR ACS grade) were from EMD Chemicals. SnO\(_2\):F electrodes were purchased from MTI corporation with a SnO\(_2\):F coating layer of <200 nm and a resistivity of 12−14 ohm/sq. Water was purified by Nanopure II system to a resistivity of >17.5 MΩ/cm.

**WO\(_3\) electrode preparation.— WO\(_3\) nanoparticles of 500 nm in diameter 50 nm in thickness and nanoparticles of 30 nm diameter were synthesized with and without the addition of PEG 8000 respectively, according to a published procedure by Augustynski.\(^ {15,27}\) The precursor solution of tungstic acid was prepared by passing 5 mL of 0.5 M sodium tungstate (Na\(_2\)WO\(_4\)) aqueous solution through a proton exchange column packed with 20 mL of protonated Dowex 50 W−X8 resin. For WO\(_3\) nanoparticles synthesized with no PEG, the yellow eluate of tungstic acid precursor was collected in water and aged with constant stirring for one day and used within three weeks to fabricate electrodes by dropcasting 0.2 ml of the precursor solution (equivalent to a concentration of 2.5 mg/ml WO\(_3\)) onto SnO\(_2\):F substrates at 100°C. This typically produces WO\(_3\) nanoplate films with a thickness of 2 μm. For WO\(_3\) nanoparticles synthesized with PEG, the yellow eluate of tungstic acid precursor was collected in ethanol and 1.15 g of PEG 8000 was added immediately as a stabilizer to control particle size and prevent aggregation. The ratio of WO\(_3\) to PEG was kept at 0.5 w/w, as suggested.\(^ {15}\) The viscous pale yellow precursor solution with PEG 8000 was completely stirred and used within a week to fabricate electrodes by dropcasting 0.2 ml of the precursor ethanol solution (equivalent to a concentration of 2.5 mg/ml WO\(_3\)) onto SnO\(_2\):F substrates at 100°C. The yield WO\(_3\) nanoparticle films are 300 nm in film thickness and composed of particles with 30 nm average diameter. A thicker film of 30 nm WO\(_3\) was also prepared by repetitively applying 0.2 ml of the precursor solution (equivalent to a concentration of 2.5 mg/ml WO\(_3\)) and drying at 100°C until thickness reaches 2 μm. To achieve this, a total amount of 4 mg WO\(_3\) was used. As a comparison, bulk WO\(_3\) particles were also investigated in this study. 600 nm-thick films of bulk WO\(_3\) particles were prepared by sonicating bulk WO\(_3\) powders in water and dropcasting 0.2 ml of 2.5 mg/ml bulk WO\(_3\) suspension onto SnO\(_2\):F substrates at 100°C. All SnO\(_2\):F substrates (1.0 × 2.5 cm\(^2\)) were pre-cleaned by consecutive
sonications in acetone, methanol, and isopropyl alcohol, followed by a final rinse with water. All WO₃ films are of 1.0 × 1.0 cm² area and annealed at 500 °C for 30 min before testing. This step converts WO₃ nanocrystals into the desired monoclinic structure, and allows the removal of PEG 8000 in the case of 30 nm WO₃ nanoparticles.

Characterization.— Transmission electron microscopy (TEM) images of WO₃ nanoparticles were taken with a Philips CM-12 transmission electron microscope at an accelerating voltage of 120 kV. To prepare TEM samples, WO₃ nanoparticles were scratched off from the electrodes and suspended in water. Particle dispersions were drop-casted onto copper grids with carbon film coating, and air dried. Scanning electron microscopy (SEM) images of WO₃ film were obtained on a FEI XL30-SPFEG high-resolution scanning electron microscope at an operating voltage of 5 kV. Thickness of the films was verified by Veeco Dektak profilometer. UV-Vis diffuse reflectance spectra of WO₃ film on SnO₂:F electrode were recorded using a Thermo Scientific Evolution 220 UV-Vis spectrometer equipped with an integrating sphere. The reflectance data were converted to Kubelka-Munk function as f(R) = (1 - R)²/2R and plotted versus wavelength. Tauc plot analysis was performed with the obtained diffuse reflectance spectra by plotting (hν · f(R))² or (hν · f(R))¹/² versus photon energy hν in the unit of eV. Powder X-ray diffraction (XRD) patterns were recorded on a Scintag XDS2000 powder X-ray diffractometer equipped with Cu Kα as the X-ray source at a wavelength of λ = 0.154 nm with 2 mm tube slit divergence, 4 mm scatter, 0.5 mm column scatter, and 0.2 mm receiving widths.

Photoelectrochemical measurements.— Electrochemical and photoelectrochemical measurements were performed in a conventional three-electrode cell with a quartz front window, a KCl-bridged saturated calomel electrode (SCE) as the reference electrode, a Pt foil as the counter electrode, and a WO₃ film on SnO₂:F as the working electrode. Unless stated otherwise, 50 mL of 0.1 M K₂SO₄ electrolyte solution with a pH of 3.5 was used and degassed with N₂ prior to the measurements. Photocurrent scans were recorded by scanning potential in the cathodic direction with a scan rate of 10 mV/s under chopped light illumination, using a Gamry Reference 600 potentiostat. Unless stated otherwise, no special polarization or conditioning was applied to the electrodes prior to each photocurrent scan, except for a 5 s brief stirring of solution applied between successive scans. Illumination was provided by a 300 W Xe arc lamp connected to the cell through a SiO₂ fiber-optic cable (50 ± 10 mW/cm² at the electrode front as measured by an International Light IL1400BL photometer equipped with a GaAsP detector for 280–660 nm range). Anodic linear sweep was performed from 0.9 V to 2.3 V versus RHE. Mott-Schottky measurements were carried out in 0.1 M K₂SO₄ aqueous electrolyte solution with a pH of 3.5 by H₂SO₄ and H₂O₂ and conducted in dark from +1.30 V to +0.50 V vs. RHE at a frequency of 10 Hz, a voltage step of 0.05 V and an AC voltage amplitude of 2 mV/rms. Electrochemical impedance spectra (EIS) were measured at a frequency of 10 Hz, a voltage step of 0.05 V and an AC voltage amplitude of 2 mV/rms. Electrochemical impedance spectra (EIS) were measured at an AC voltage amplitude of 2 mV, a frequency range of 0.1–10⁶ Hz and Xe arc lamp illumination of 50 ± 10 mW/cm². Equivalent circuit model fitting of EIS data was achieved using Gamry Echem Analyst software. All the potential readings were calibrated using the standard potential of K₃[Fe(CN)₆] as +0.358 V vs. RHE, and reported on the Relative Hydrogen Electrode (RHE) scale by shifting 0.21 V anodically from the Normal Hydrogen Electrode (NHE) scale to account for the pH condition of 3.5.

Results and Discussion

Properties.— Tungsten trioxide (WO₃) nanoplates with an average diameter of 500 nm and a thickness of 50 nm (Figure 1A) were prepared following an established procedure by Augustynski.13 WO₃ films (Figure 1B) were fabricated by dropcasting tungstic acid precursor solution on SnO₂:F substrates at 100 °C and annealing at 500 °C. The crystal phase of WO₃ transforms to orthorhombic upon heating to 500 °C, but changes to monoclinic γ-WO₃ once it is cooled to room temperature,10 which agrees with the XRD pattern in Figure 1C. Film thickness was controlled at 2.0 ± 0.5 μm and kept consistent among WO₃ nanoplate samples, as verified by thickness profilometry measurements. UV–vis diffuse reflectance spectrum and Tauc plots of the film are shown in Figure 1D and 1E. An indirect bandgap of 2.6 eV and a direct bandgap of 2.9 eV are observed, in good agreement with the literature values reported for monoclinic WO₃.38,39 Besides, an additional broad absorption peak in the infrared region is observed and is attributed to the electron transfer from W⁶⁺ to W⁵⁺ at the oxygen-deficient sites in the structure.10 This oxygen deficiency makes WO₃ nonstoichiometric and intrinsically n-type.

Enhanced photoelectrochemical performance.— A typical photocurrent scan from +1.37 V to +0.47 V vs. RHE is shown in Figure 2A for a WO₃ nanoplate photoanode immersed in 0.1 M K₂SO₄ aqueous solution at pH 3.5. The onset of anodic photocurrent is observed at +0.53 V vs. RHE, consistent with previous studies.12,40 This photocurrent reaches 110 μA/cm² at 1.36 V vs. RHE during the first scan, but continuously decays in subsequent scans. This is due to the accumulation of peroxide intermediates on WO₃ surface during water oxidation.41 Although water oxidation to oxygen is energetically favorable, it is kinetically slow and subject to other competing redox reactions, incl. the formation of peroxide intermediates.42 However, when the photocurrent scans were performed down to +0.17 V vs. RHE instead of +0.47 V vs. RHE, a continuous increase in photocurrent was observed in subsequent scans (Figure 2B). The maximum increase of 10-fold was achieved after four scans. This increase is accompanied by the cathodic reduction current at potentials below +0.45 V (see arrow in Figure 2B). Therefore, the improved photocurrent is attributed to the reduction below +0.45 V. Indeed, when a fresh WO₃ film is subjected to the reducing potential of +0.17 V vs. RHE for 60 s, a near 10-fold increase of photocurrent in the subsequent scans is observed (Figure S1A). This enhancement from the reduction treatment is independent on the directionality of the photocurrent.
Figure 2. (A) Repetitive photocurrent scans from +1.37 V to +0.47 V vs. RHE for a WO$_3$ nanoplate photoanode in 0.1 M K$_2$SO$_4$ aqueous solution at pH of 3.5 as adjusted by H$_2$SO$_4$. (B) Repetitive photocurrent scans from +1.37 V to +0.17 V vs. RHE for an identical WO$_3$ nanoplate photoanode in the same electrolyte condition. A reduction feature below +0.5 V was observed and indicated by the black arrow. All scans were performed at a scan rate of 10 mV/sec under Xe full spectrum illumination of 50 ± 10 mW/cm$^2$.

scans (Figure S1B). Also, longer reduction treatment, e.g. 120 s, does not lead to a further increase in photocurrent.

In order to test the stability of this reduction activated WO$_3$ film against oxidative corrosion, photocurrent scans were performed after exposing the activated film to air for 60 min and after heating the activated film to 100 °C. Figure S2A shows that air exposure at room temperature does not lead to any noticeable deactivation of the film. The slight decrease in photocurrent results from the accumulation of peroxo-intermediates,$^{27}$ as seen previously in Figure 2A. On the other hand, 30 min heating of the film in air (O$_2$ source) completely reverses the photocurrent enhancement (Figure S2B), but the same film can be fully re-activated by another 60 s reduction at +0.17 V. This suggests that the lattice W$^{6+}$ to W$^{5+}$ conversion is reversible and can be controlled by reductive and oxidative treatments. Chronoamperometry (Figure 3A) was measured to evaluate the effect of reduction on the photocorrosion behavior of WO$_3$ films. In the absence of reduction treatment, only 9% of the photocurrent (at +1.15 V applied potential) remains after one hour, but with reduction activation, 49% remains after 1 hr of operation. This enhancement is likely due to the presence of substoichiometric WO$_{3-x}$, which has been reported to resist the peroxo-species assisted photocorrosion.$^{24,42}$ Photocurrent stability is expected to improve further upon coating the WO$_3$ with an oxygen evolution cocatalyst that suppresses the peroxide formation,$^{27}$ or in the presence of an efficient hole scavenger. Figure 3B shows the chronoamperometry results of an identical WO$_3$ film in the presence of 20% v/v methanol, which enables the assessment of the intrinsic stability for a reduced WO$_3$ by preventing the peroxide formation. As seen, the enhanced photocurrent shows no decay after the reduction treatment when methanol is present. Lastly, the original photocurrent response of the film in Figure 3A can be restored with another reduction cycle at the end of the scan (Figure S3). These results illustrate the versatility and robustness of the reduction treatment.

Mechanism.— Dark electrochemical anodic scans on the as-prepared and reduced WO$_3$ films in Figure 4A rule out the possibility that the increase of photocurrent is a result of the change in the water oxidation kinetics. The observed onsets of +1.85 V vs RHE for water oxidation, which agrees with the literature value of +1.9 V for a pristine monoclinic WO$_3$ film,$^{14,18,37,39}$ remain independent on the electrochemical reduction treatment. The groups of Lewis$^{44}$ and Choi,$^{44}$ recently reported that water oxidation is occurring in competition with sulfate oxidation at the illuminated WO$_3$ surface. To determine if this reduction-improved photocurrent is sulfate-specific, photocurrent scans were repeated in various electrolytes, incl. 0.1 M KNO$_3$, 0.1 M KCl and 0.1 M K$_2$SO$_4$ with 20% v/v methanol (Figure S4). A similar photocurrent enhancement is observed in all cases, suggesting that the enhancement is due to an intrinsic change in the WO$_3$ films, not the electrolyte.

The reduction treatment of WO$_3$ is accompanied by a slight change in the color of the WO$_3$ films. The initial pale yellow film turns bluish yellow, blue, and then black after deep reduction, due to the appearance of a broad optical absorbance above 500 nm (Figure 4B). This change, well known as the electrochromic effect of WO$_3$, has been

Figure 3. Chronoamperometry of a WO$_3$ nanoplate film before versus after the reduction activation at an applied potential of +1.17 V vs. RHE in (A) 0.1 M K$_2$SO$_4$ aqueous solution at pH = 3.5 and (B) 0.1M K$_2$SO$_4$ aqueous solution at pH = 3.5 with the presence of 20% v/v methanol as an efficient hole scavenger to enhance photocurrent and prevent peroxide formation. Illumination source: 50 ± 10 mW/cm$^2$ unfiltered Xenon irradiation.
WO3 film in 0.1 M K2SO4 aqueous solution at pH 3.5 by H2SO4. Cation intercalation is reversible in nanostructured WO3, allowing the delocalization to occur with an applied oxidative potential.15,45 This appears as a negative dark current in subsequent anodic potential scans.33,46 Indeed, a small (−10 μA/cm²) cathodic current can be observed in close-ups of the photoelectrochemical scans (Figure S5), which supports proton intercalation and de-intercalation. More importantly, the highest photocurrent is only observed in the mildly reduced pale yellow WO3 film, whereas the strongly reduced deeply colored films produce low photocurrents (Figure 4C). This verifies that the increased photon absorption for electrochromism is not responsible from the enhancement in photocurrents.

To determine if a change of carrier concentration is responsible for the improve photocurrent of WO3 nanoplates, Mott–Schottky plots were recorded for the same WO3 film before and after reduction (Figure 5A). Positive slopes are seen in both cases, as expected for n-type WO3.24 This deviation from the classical Mott–Schottky equation24 for the as-prepared and electrochemically reduced WO3 film, respectively. This confirms the increase of carrier concentration in the reduced sample. We also note that the values are one order of magnitude lower than those previously observed by Yat Li’s group for as-prepared (1.0 × 10²² cm⁻³) and hydrogen treated WO3 nanocrystals (5.0 × 10²² cm⁻³).24 This deviation is likely due to the difference in preparation conditions of these WO3 samples.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to characterize charge transfer processes in nanostructured WO3 films.39,50 Before reduction, two semi-circles are observed in the Nyquist plot (Figure 5B), indicating two limiting charge transfer processes with distinct time constants (radii) in the as-prepared WO3 nanoplate film. The first arc with the smaller radius is assigned to electron transport through the film, whereas the second arc with the larger radius is related to the interfacial charge transfer at the WO3–electrolyte interface. After a 60 s reduction at +0.17 V, the first arc is mostly suppressed and the diameter of the second arc becomes smaller, implying improved electron transport through the film as a direct outcome of the reduction. The equivalent circuit fitting to the model shown in Figure 5B inset yields the parameters given in Figure S6. Two significant changes are observed. The film resistance term Rbulk is reduced from 242 Ω to 142 Ω. This confirms that reduction allows a better conductivity in the WO3 film. In addition, a significant increase in Cbulk (8.7 × 10⁻⁶ F to 2.5 × 10⁻⁴ F) is observed after the reduction treatment, owing to the increased carrier concentration. The rise in carrier concentration not only increases the space charge region capacitance, but also reduces the space charge region thickness.51 With the carrier concentrations determined from Mott–Schottky plots in Figure 5A and a flatband potential of +0.55 V for WO3, space charge widths of 18 nm and 0.5 nm are calculated for...
WO₃ nanofilms before and after reduction, respectively, at an applied potential of +0.8 V.⁵¹

Front versus back illumination experiments can be useful to evaluate the resistance losses in nanostructured photoelectrodes.⁴⁰,⁵² Figure 6A shows the photocurrent responses of an as-prepared WO₃ film. Back illumination provides a higher photocurrent than front illumination, suggesting that photocurrent from front illumination is limited by electron transport through WO₃ film and collection at the back substrate. Figure 6B compares the front vs back illumination on the same film after reduction. Front illumination now produces higher photocurrent, indicating that electron transport and collection no longer limits the photocurrent. This is a result of the increased carrier concentration and film conductivity from the reduction treatment. Now back illumination produces 25% less photocurrent after reduction, due to photon reflection and absorption losses by the SnO₂:F substrate.

In summary, the results in Figure 4–6 reveal that the reduction-induced enhancement in WO₃ is due to the increase of carrier concentration (Figure 5A) and film conductivity (Figure 5B), which improves the majority charge collection in the film. This electrochemical doping enhancement is analogous to that observed in CdSe nanocrystal films⁵³ and for films made of anatase TiO₂ particles,⁴¹ TiO₂ nanotubes,⁵⁵ and for SrTiO₃.⁵⁶ For WO₃, the effect relies on the creation of shallow photoinjectors of 200 μm–200 μm WO₃ particles before and after reduction, respectively, at an applied potential of +0.8 V.⁵¹

Particle size dependency.— To investigate the dependency of electrochemical doping on particle size, photoelectrodes made of two additional WO₃ sizes were also studied. According to SEM (Figure 7A–7B), commercial WO₃ consists of large 20 μm aggregates of 200 nm-diameter crystals. Separately, 30 nm WO₃ nanoparticles (Figure 7C–7D) were prepared by acidification of 0.5 M Na₂WO₄ in the presence of PEG 8000.¹³,¹⁵,⁴⁰ Photoanode films were cast from these particle precursors following the same preparation used for the previous 500 nm wide 50 nm thick nanoplates. The corresponding photocurrent responses are shown in Figure 8B–8C in comparison to that of the 50 nm thick nanoplates in Figure 8A. For the as-prepared films, photocurrents are found to depend inversely on particle size (as summarized by the solid-filled columns in Figure 8E), i.e. the smallest 30 nm particles give the largest photocurrent of 0.013 mA/cm² at 0.200 mA/cm², followed by that of the 50 nm nanofilms (10 times) and 30 nm nanoparticles (2 times). This trend reflects the notion that majority carrier transport for the 200 nm–20 μm particles occurs predominantly through crystal domains, while for the 30 nm particles it occurs mostly by hopping from crystal to crystal.⁵⁶ Thus, the large crystals are more sensitive to a change in crystal conductivity. However, with both majority and minority carrier transport optimized, light absorption can become a limiting factor for the photocurrent. This is the reason for the lower performance of the reduced 30 nm film sample, which due to reduced light scattering has a nearly transparent optical appearance (Figure 8D). Using this insight, a thicker (2 μm) film was fabricated from 4 mg of the 30 nm diameter WO₃ nanoparticles. After a brief in-situ reduction treatment, this film delivers 3.8 mA/cm² photocurrent at +1.36 V vs. RHE under Xe full spectrum of 50 ± 10 mW/cm² (Figure 8D). This is close to the highest observed water oxidation performance of the reduced 30 nm film sample, which due to reduced light scattering has a nearly transparent optical appearance (Figure 8D). Using this insight, a thicker (2 μm) film was fabricated from 4 mg of the 30 nm diameter WO₃ nanoparticles. After a brief in-situ reduction treatment, this film delivers 3.8 mA/cm² photocurrent at +1.36 V vs. RHE under Xe full spectrum of 50 ± 10 mW/cm² (Figure 8D). This is close to the highest observed water oxidation performance.
Figure 8. Photocurrent scans before and after a sequential reduction at $+0.17\text{V}$ vs. RHE for (A) a film of 0.5 mg WO$_3$ nanoplates of 500 nm in diameter and 50 nm in thickness, (B) a film of 0.5 mg WO$_3$ bulk particles of 200 nm–20 μm, (C) a film of 0.5 mg WO$_3$ nanoparticles of 30 nm in diameter and (D) a film of 4 mg WO$_3$ nanoparticles of 30 nm in diameter. All scans were conducted from $+1.37\text{V}$ to $+0.47\text{V}$ with a scan rate of 10 mV/sec V in 0.1 M K$_2$SO$_4$ aqueous solution at pH = 3.5 under Xe full spectrum illumination of 50 ± 10 mW/cm$^2$. (E) Histogram of photocurrent enhancement observed at $+1.36\text{V}$ vs. RHE in Figure 8A–8D for various WO$_3$ systems of diverse sizes and film thicknesses.

photocurrents reported for WO$_3$ films (>2.5 mA cm$^{-2}$, AM 1.5, $E_{\text{App}}$ = +1.0 V vs. NHE). The high performance is remarkable, considering that no other optimization, e.g. nanowire geometry, nor water oxidation electrocatalyst were utilized in the fabrication of this photoanode. It demonstrates that minority carrier injection, majority carrier transport, and light absorption are the main factors that control the performance WO$_3$ nanoparticle electrodes.

**Conclusions**

In summary, we demonstrate that electrochemical doping enhances the photoelectrochemical performance of WO$_3$ photoanodes by up to one order of magnitude. Doping raises the majority carrier concentration and lowers the charge transport resistance of the film. The enhancement remains active in WO$_3$ electrodes upon air exposure, but can be undone by heating in air. Electrochemical doping is the most effective for photoelectrodes with large WO$_3$ crystals, where charge transport occurs through crystal domains, and less effective for electrodes of small WO$_3$ particles, where majority carrier transport occurs through hopping between particles. The understanding of majority carrier transport can be used to achieve a record performance of WO$_3$ photoanodes (3.8 mA/cm$^2$ at $+1.36\text{V}$ vs. RHE under Xe full spectrum of 50 ± 10 mW/cm$^2$), after minority carrier extraction and light absorption are also optimized separately via particle size and film thickness. These findings will be of use for the optimization of photoelectrochemical devices in general.
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