

An Electrochemical Method to Enhance the Performance of Metal Oxides for Photoelectrochemical Water Oxidation

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Experimental Section

Synthesis of Rutile TiO₂ nanowires: Rutile TiO₂ nanowire arrays were grown on a fluorine-doped tin oxide (FTO) glass substrate using a reported hydrothermal method.¹ 0.5 mL titanium n-butoxide was mixed with 15 ml of concentrated hydrochloric acid and 15 ml deionized (DI) water in a 50 ml beaker. After the solution became clear, the solution mixture were transferred to a Teflon-lined stainless steel autoclave (40 ml volume), where the FTO substrate was submerged in the solution with conducting side facing down. The sealed autoclave was kept at 150 °C for 5 hours, and then cooled down to room temperature. When taking out the FTO glass, a white film was uniformly coated on the FTO glass. The sample was finally washed with deionized water. Before TiO₂ was used for PEC studies, the TiO₂ film was annealed at 550 °C in air for 3 hours.

Synthesis of WO₃ nanoblocks: WO₃ nanoblocks were grown on a FTO glass substrate using a modified seed mediated solvothermal method.² The WO₃ seed solution was prepared as follows: 0.5 mmol WCl₆ was dissolved in 20 ml ethanol solution; the dissolved WCl₆ was quickly hydrolyzed by water moisture and produced blue precipitates. 30% H₂O₂ solution was added into the blue precipitate-containing solution with stirring until the solution became clear. This WO₃ seed solution was dropped onto a piece of clean FTO glass. The excess solution was blow away by compressed air after 30 s. The FTO substrate was then annealed at 350 °C on a hot plate in air for 10 min. Repeat this deposition-annealing process for two or three times to get a uniform WO₃ seed layer on FTO substrate. Meanwhile, 0.2 g Na₂WO₄ was dissolved in 25 ml mixture of ethylene glycol and water (volume ratio: 1:5) and the pH of the solution was adjusted to 2 by

adding hydrochloric acid. The prepared solution was transferred to a 30 ml volume Teflon-lined stainless steel autoclave. The WO_3 seeded FTO substrate was placed into the Teflon-lined stainless steel autoclave with the seeded side facing down. The sealed autoclaves was heated in an electric oven at $150\text{ }^\circ\text{C}$ for 5 hours, and then cooled down to room temperature naturally. The seeded FTO substrate was coated with a uniform blue film. After washed with ethanol and water, the film was calcined in the air at $500\text{ }^\circ\text{C}$ for 2 hours.

Synthesis of anatase TiO_2 nanowires: Anatase TiO_2 nanowires were prepared on a titanium foil by using a previously reported hydrothermal method.³ A clean Ti foil was placed in a Teflon-lined stainless-steel autoclave filled with an aqueous 1 M NaOH solution. The sealed autoclave was kept at $180\text{ }^\circ\text{C}$ for 7 h. After the autoclave cooled to room temperature, the Ti foil was taken out and washed with DI water. The Ti foil was covered with nanowires and was immersed in an aqueous 1 M HCl solution for 10 min, rinsed with DI water, and air-dried. Finally, the Ti foil with nanowires was annealed in air at $500\text{ }^\circ\text{C}$ for 3 h.

Synthesis of BiVO_4 nanoparticle film: 1 mmol NH_4VO_4 , 1 mmol BiVO_4 and 2.5 mL concentrated HNO_3 was mixed together in 50 ml deionized water. Ammonium hydroxide was used to neutralize the mixed solution, until no precipitate was produced with a pH around 9. Then, the precipitate was centrifuged out. The as prepared bright yellow precipitate was dispersed in 30 ml ethanol solution with addition of 0.2 g polyvinylpyrrolidone to increase viscosity for spin coating precursor. A piece of FTO

glass was cleaned with ethanol, acetone and water respectively. 0.2 ml precursor solution was dropped on the FTO glass, wait 30 seconds and then spin coating at 1500 r/min. the deposited FTO glass was annealed at 400 °C for 15 min to remove organic binder. Then repeat this process for 6 times and finally the obtained unformed film was air annealed at 550 °C for 2 h.

Synthesis of ZnO nanowires: ZnO nanowire arrays on FTO glass was synthesized by a modified seed mediated synthesis.⁴ The seed coating was achieved by annealing the zinc acetate ethanol solution film on FTO glass at 350 °C for 30 min. This coating step was repeated three times. The seed coated FTO glass was placed into a Telfon-lined stainless steel autoclave with seeded side facing down, filled with 20 ml 0.05 M zinc nitrate and 0.05 M hexamethylenetetramine aqueous solution. The sealed autoclave was heated in an electric oven at 90 °C for 6 hours.

Material characterization: Scanning electron microscopy (SEM) images were collected with a field-emission SEM (Hitachi S-4800 II). X-ray diffraction (XRD) spectra were collected with a Rigaku Americas Miniflex Plus powder diffractometer. Diffraction spectra were recorded from a 2θ angle of 20 to 80 degree with a step size of 0.04 degree at a rate of 1 degree/min. X-ray Photoelectron Spectroscopy (XPS) was performed on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) using Al-monochromatic X-ray at a power of 25 W with an X-ray-beam diameter of 10 mm, and a pass energy of 29.35 eV. The pressure of analyzer chamber was maintained below 5×10^{-8} Pa during the measurement. The binding energy was calibrated using the C 1s photoelectron peak at

284.6 eV as the reference. UV-vis diffusive reflectance measurement was conducted on Shimadzu UV-3101 PC UV-vis-NIR scanning spectrophotometer equipped with an integrating sphere attachment.

Electrochemical treatment: Electrochemical treatment was conducted on a CHI 660D electrochemical workstation. For TiO₂ nanowire arrays (rutile and anatase), a potential of -1.8 V vs. Ag/AgCl was applied in a 1 M NaOH aqueous solution for 10 s. For WO₃ nanoblocks, a potential of -0.8 V vs. Ag/AgCl was applied in a 1 M H₂SO₄ aqueous solution for 3 s and the color of WO₃ was quickly converted from light yellow to blue. Then the film was annealed on a hot plate for another 5 min at 300 °C. For BiVO₄ nanoparticle film, a potential of -0.8 V vs. Ag/AgCl was applied in a 0.5 M Na₂SO₄ aqueous solution for 30 s. For ZnO nanowire arrays, a potential of -1.2 V vs. Ag/AgCl was applied for 30 s in the neutral Na₂SO₄ electrolyte solution. Mott-Schottky measurements of WO₃ were conducted on electrochemical workstation (CHI-660D) with 5 mV perturbation at a frequency of 10000 Hz in in the neutral Na₂SO₄ electrolyte solution. The donor density was derived from the Mott-Schottky equation,

$$N_d = (2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1},$$

where e_0 is the electron charge, ϵ the dielectric constant of WO₃ ($\epsilon=20$), ϵ_0 the permittivity of vacuum, N_d the donor density, and V the applied bias at the electrode. The equation was used to calculate is re-oxidation time based on enhanced photocurrent:

$$T_{\text{re-oxidation}} = \frac{\int_0^3 I(t)dt}{I_{\text{enhanced photocurrent}}},$$

where $T_{\text{re-oxidation}}$ is the re-oxidation time, $I(t)$ is the electrochemical reduction $I-t$ curve

and $I_{\text{enhanced photocurrent}}$ is the enhanced photocurrent at specific potentials.

Photoelectrochemical measurements: Metal oxide nanostructures were fabricated into photoanodes by soldering a copper wire onto a bare part of the FTO (Ti foil) substrate. The substrate edges and the metal contact region were sealed with insulating epoxy resin. The working electrode area is in the range of 0.15-0.2 cm². 1 M NaOH aqueous solution (pH = 13.6) was used as a PEC electrolyte for Rutile and Anatase TiO₂ nanowires. 0.5 M Na₂SO₄ aqueous solution (pH=6.8) was used as electrolyte for WO₃ and BiVO₄. Linear sweeps, *I-t* scans and electrochemical impedance spectra were collected by a CHI 660D electrochemical station, with Ag/AgCl as reference and Pt wire as counter electrode, under simulated sunlight with a 150 W xenon lamp (Newport 6255) coupled with an AM 1.5 global filter (Newport 81094). Incident-photon-to-current-conversion-efficiencies (IPCE) were collected in the same electrolyte used for linear sweeps and *I-t* measurements by CHI 660D electrochemical station with a solar simulator (Newport 69920, 1000 W xenon lamp), coupled with an infrared water filter (Oriol 6127) and aligned monochromator (Oriol Cornerstone 130 1/8 m). Charge injection efficiency is estimated by measuring the photocurrent density in 0.5 M Na₂SO₄ solution with/without H₂O₂. Charge separation efficiency is measured the photocurrent densities under 370 nm light illumination in 0.5 M Na₂SO₄ solution with H₂O₂. The enhanced factors on charge separation efficiency and injection efficiency were calculated by the equations:

$$\text{Enhanced factor (charge separation)} = \frac{\text{Charge separation efficiency}_{\text{WO}_3-x}}{\text{Charge separation efficiency}_{\text{WO}_3}}$$

$$\text{Enhanced factor (charge injection)} = \frac{\text{Charge injection efficiency}_{\text{WO}_{3-x}}}{\text{Charge injection efficiency}_{\text{WO}_3}}$$

Supplementary Figures

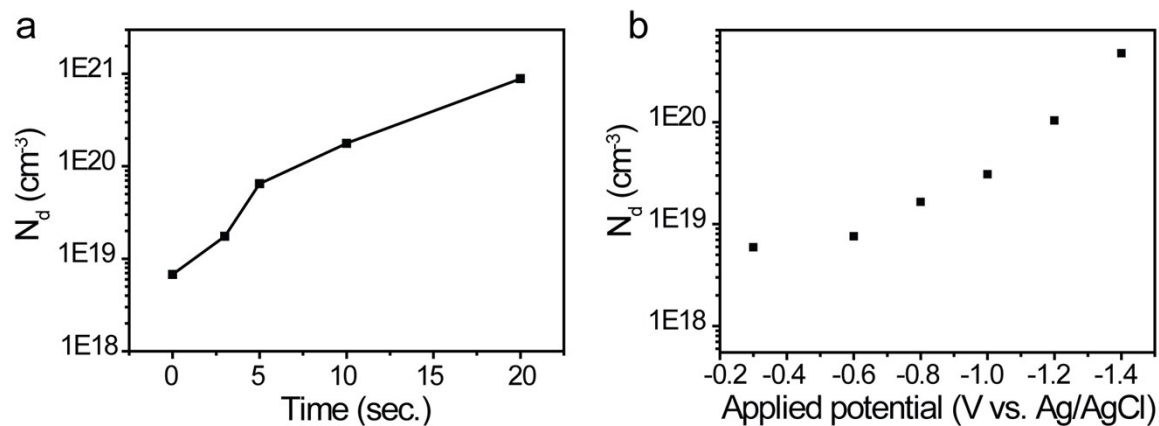


Figure S1. (a) A plot of donor density of WO_3 as a function of electrochemical reduction time at the potential of -0.8V vs. Ag/AgCl . (b) A plot of donor density of WO_3 electrochemically reduced for 3s as a function of applied potential.

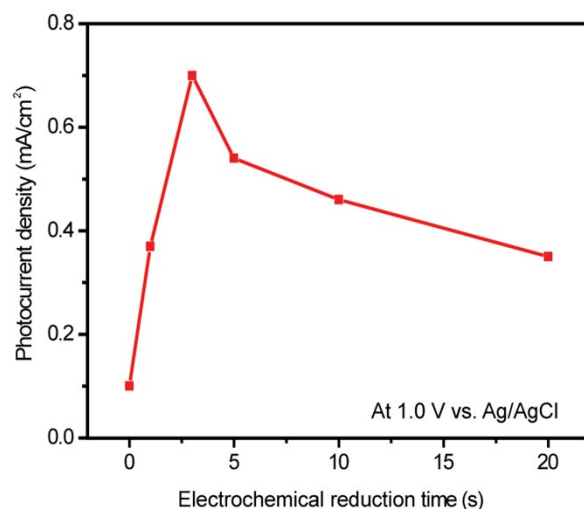


Figure S2. The photocurrent densities measured at 1.0 V vs. Ag/AgCl for WO_3

photoanodes prepared with different electrochemical reduction time.

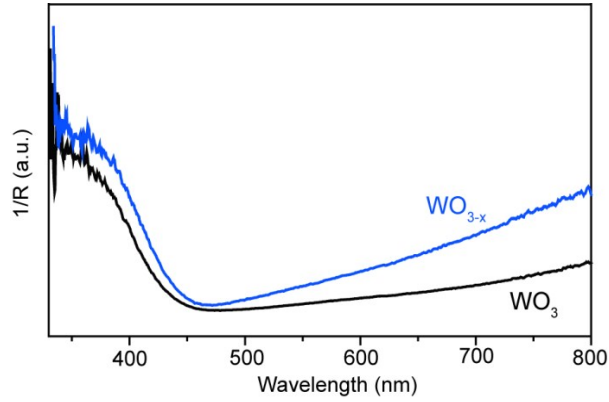


Figure S3. UV-visible diffusive reflectance spectra collected from WO₃ and WO_{3-x} samples.

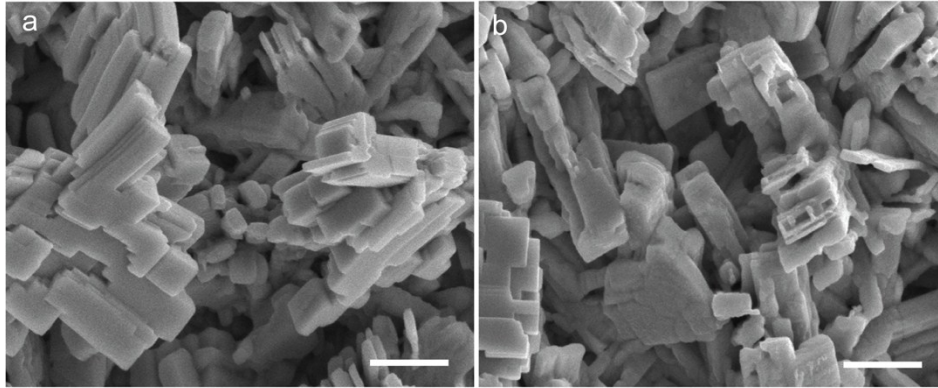


Figure S4. SEM images of WO₃ and WO_{3-x} samples. Scale bars are 1 μm.

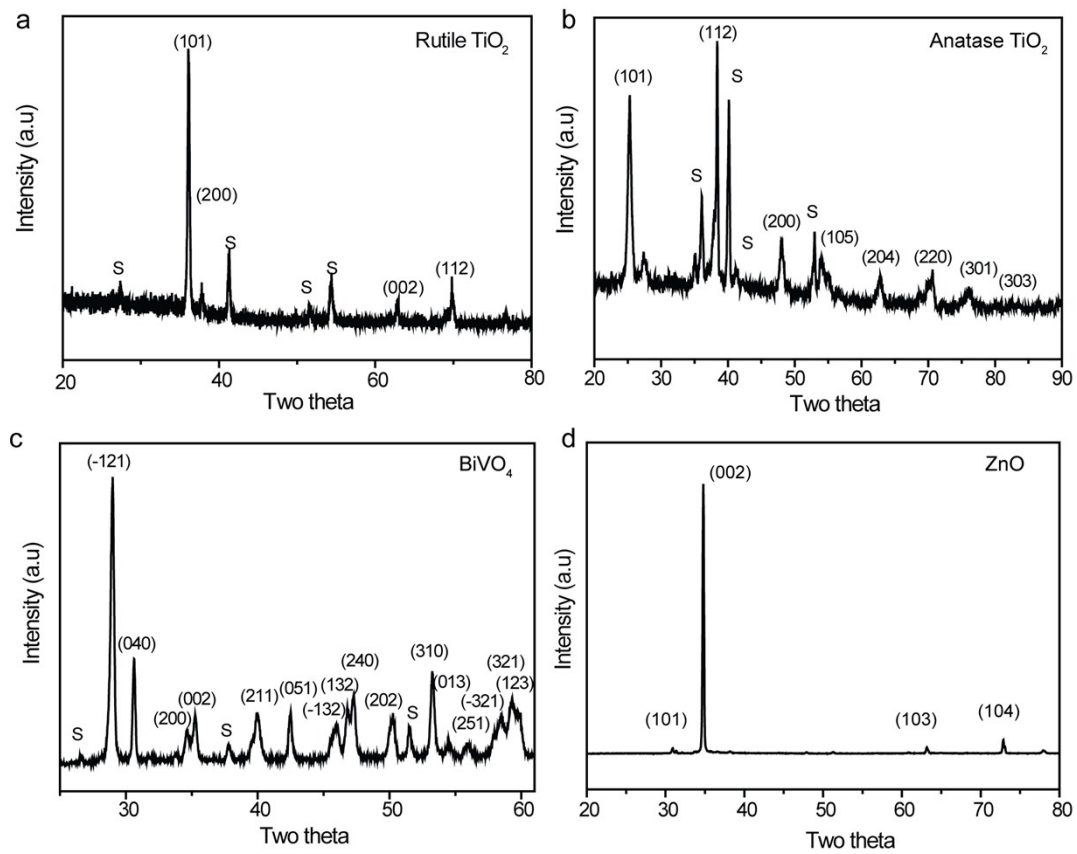


Figure S5. XRD spectra of the prepared rutile TiO_2 nanowire arrays, anatase TiO_2 nanowire arrays, BiVO_4 nanoparticle thin film and ZnO nanowire arrays.

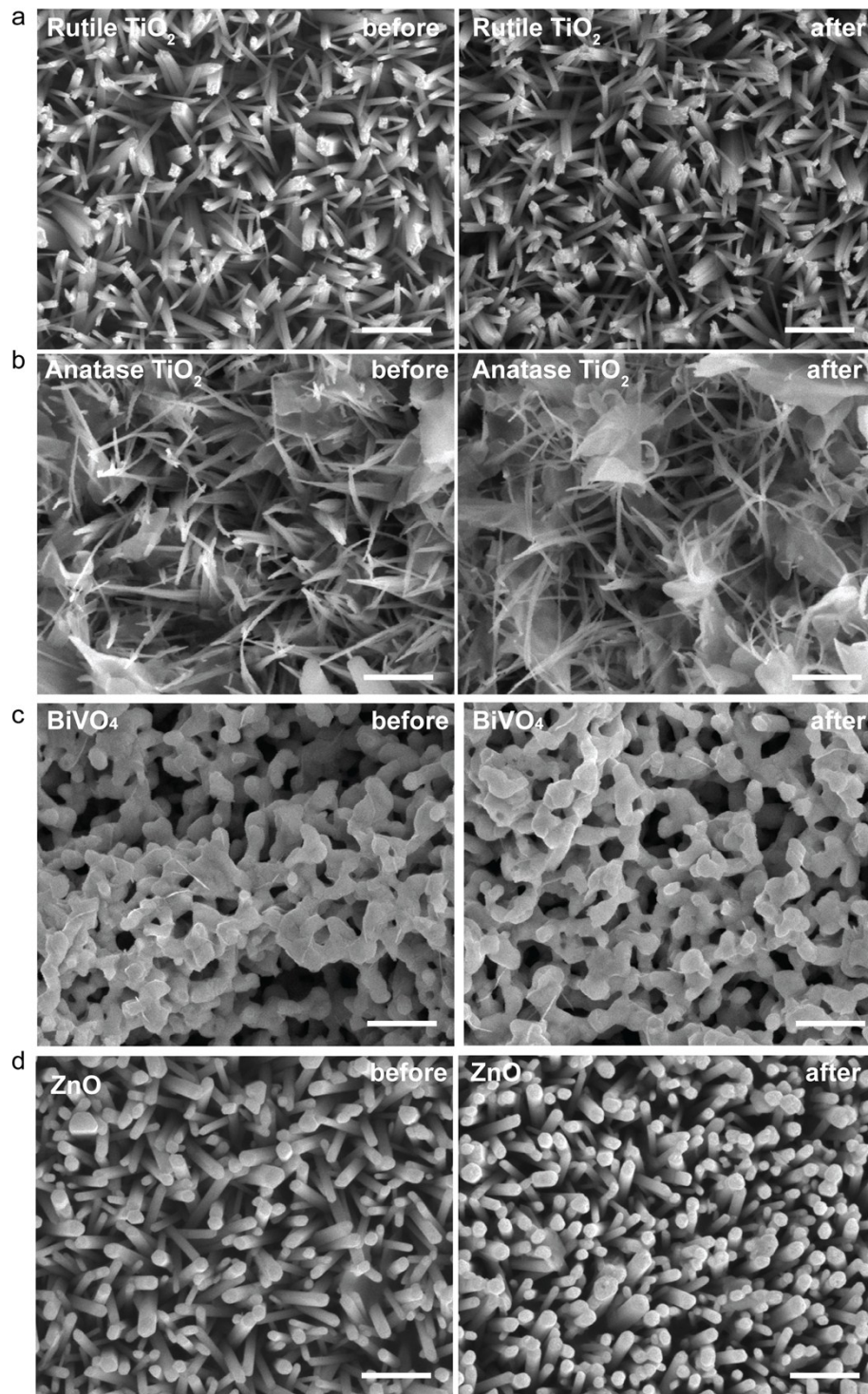


Figure S6. SEM images of rutile TiO₂ nanowire, anatase TiO₂ nanowires, BiVO₄ nanoparticles and ZnO nanowires before and after electrochemical treatment. Scale bars are 1 μm .

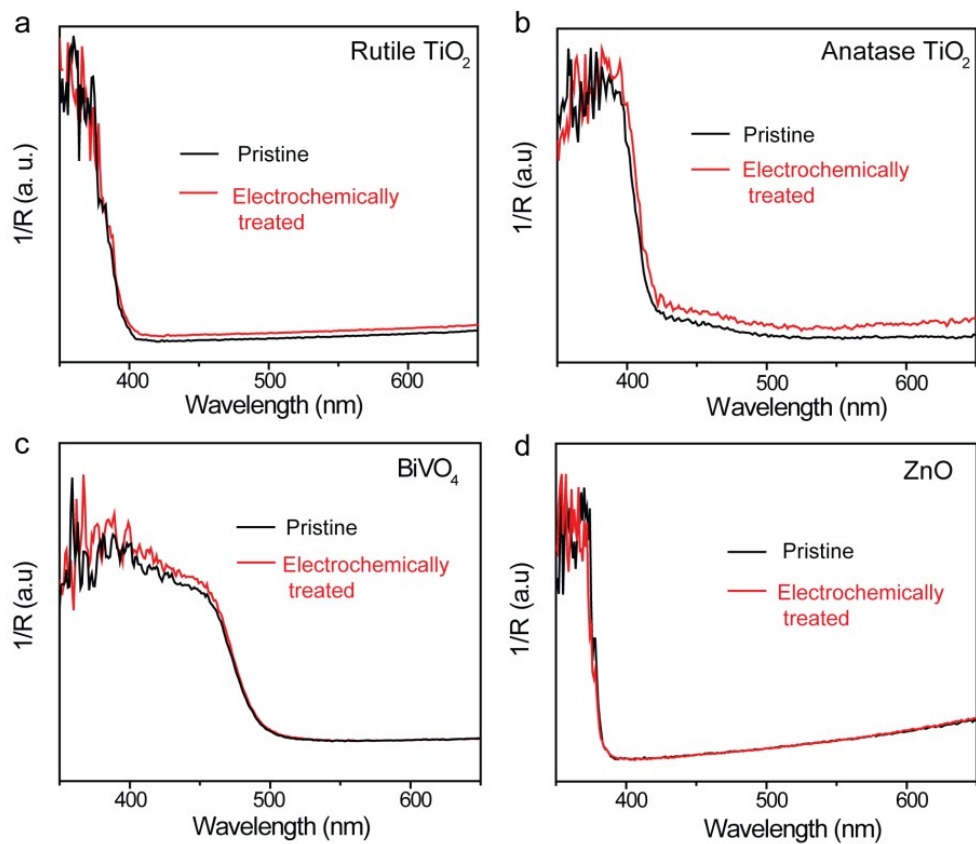


Figure S7. UV-vis diffusive reflectance spectra of rutile TiO_2 nanowire, anatase TiO_2 nanowires, BiVO_4 nanoparticles and ZnO nanowires collected before and after electrochemical treatment.

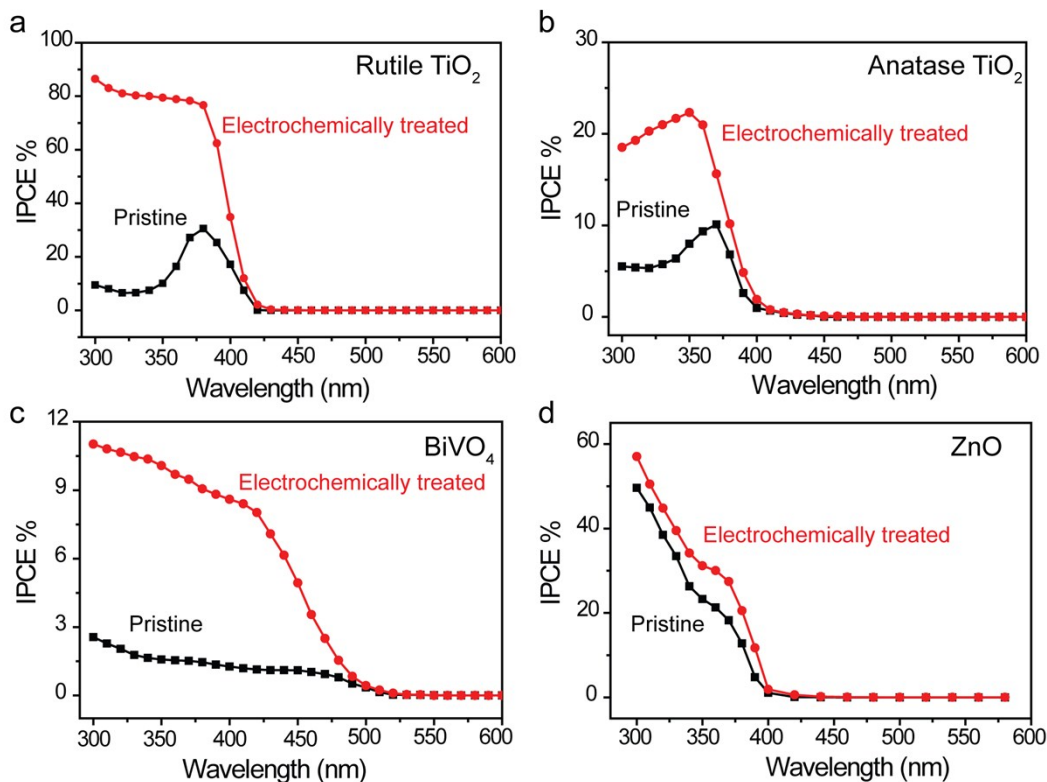


Figure S8. IPCE spectra of untreated and electrochemically treated rutile TiO_2 nanowire, anatase TiO_2 nanowires, BiVO_4 nanoparticles and ZnO nanowires.

References

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