

Supporting Online Materials

Interface Engineering by Piezoelectric Potential in ZnO-based Photoelectrochemical Anode

Jian Shi,¹ Matthew B. Starr,¹ Hua Xiang,¹ Yukihiro Hara,² Marc A. Anderson,^{2,4} Jung-Hun Seo,³ Zhenqiang Ma,³ Xudong Wang^{1,*}

¹ Department of Materials Science and Engineering, ² Department of Civil and Environmental Engineering, ³ Department of Electrical and Computer Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA. ⁴IMDEA Energy Institute, CAT-URJC, Tulipán sn, 28933 Móstoles, Spain.

* Email: xudong@engr.wisc.edu

Experimental Details:

Materials: ZnO film was deposited in a home-made RF sputtering system. Prior to deposition, the as-received ITO/PET substrate (from Multek; ITO layer is 200 nm thick and PET is 75 μm thick) was cleaned by acetone, ethanol and DI water in sequence and dried by N_2 . A 2 inch \times 2 inch substrate was used for ZnO sputtering at a pressure of 1.5×10^{-3} Torr under Ar (50 sccm) and O_2 (15 sccm) flow. The RF power for sputtering was kept at 80 W. Deposition was paused every 30 minutes for a 30-minute period to prevent overheating the substrate. The total deposition time was 150 minutes for a thickness of $\sim 1 \mu\text{m}$.

Device fabrication: The as deposited ZnO/ITO/PET sample was cut into a 20 mm \times 10 mm piece and then glued on a PMMA cantilever with dimensions of 73 mm \times 8 mm \times 1.3 mm. The cantilever was anchored on a home-made PMMA clamp, where the working area of the ZnO/ITO/PET piece is right above the clamped point. Thus, the strain experienced by ZnO can be quantified via the traditional cantilever model. The ITO electrode was wired by a highly-flexible Au wire to a fixed electrode pad where the strain is always zero, through which the working electrode port of potentiostat was connected. The Au wire and all the exposed ITO area was completely and seamlessly sealed by epoxy. Most ZnO surface was also covered by epoxy and only an area of 2 mm \times 1 mm was exposed for PEC reactions.

PZ-PEC measurement: The cantilever system was loaded into a 1L glass beaker that was half-filled with 0.5 M K_2SO_4 aqueous solution. The measurement was conducted via a three-electrode system, in which a saturated calomel electrode (SCE) was used as the reference electrode, a Pt gauze as the counter electrode, and ZnO/ITO/PET as the working electrode. Potentiostat (Solartron[®] SI 1287) was applied to control and monitor the PZ-PEC process. N_2 gas was purged through the cell during the measurement to instantaneously flush away O_2 from the working electrode and H_2 from the counter electrode. A light source was provided by a 500W Hg (Xe) arc lamp (Oriel, 66142). A liquid water filter (Oriel, 6123NS) was applied to eliminate the IR light heating effect on electrolyte. During the measurement, the ZnO side of sample was facing the light source. A speed-controlled motor with wedged shaft drove the dynamic and static bending of the PMMA cantilever. Distance between shaft and cantilever was tuned for creating different strains.

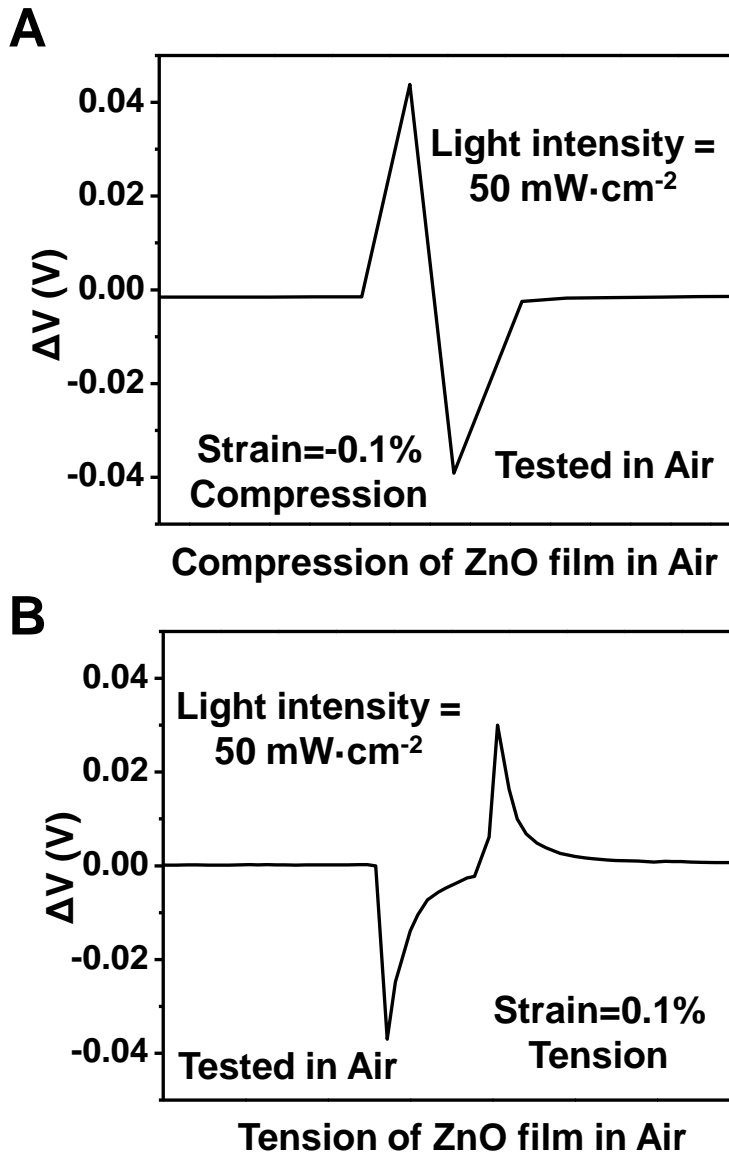


Figure S1. Piezoelectric polarization characterization. Piezoelectric potential produced by the ZnO film deposited on an ITO substrate when subjected to compressive (-0.1%) **A.** and tensile (0.1%) **B.** strain. The potential was measured in air under illumination of 50 mW cm⁻².

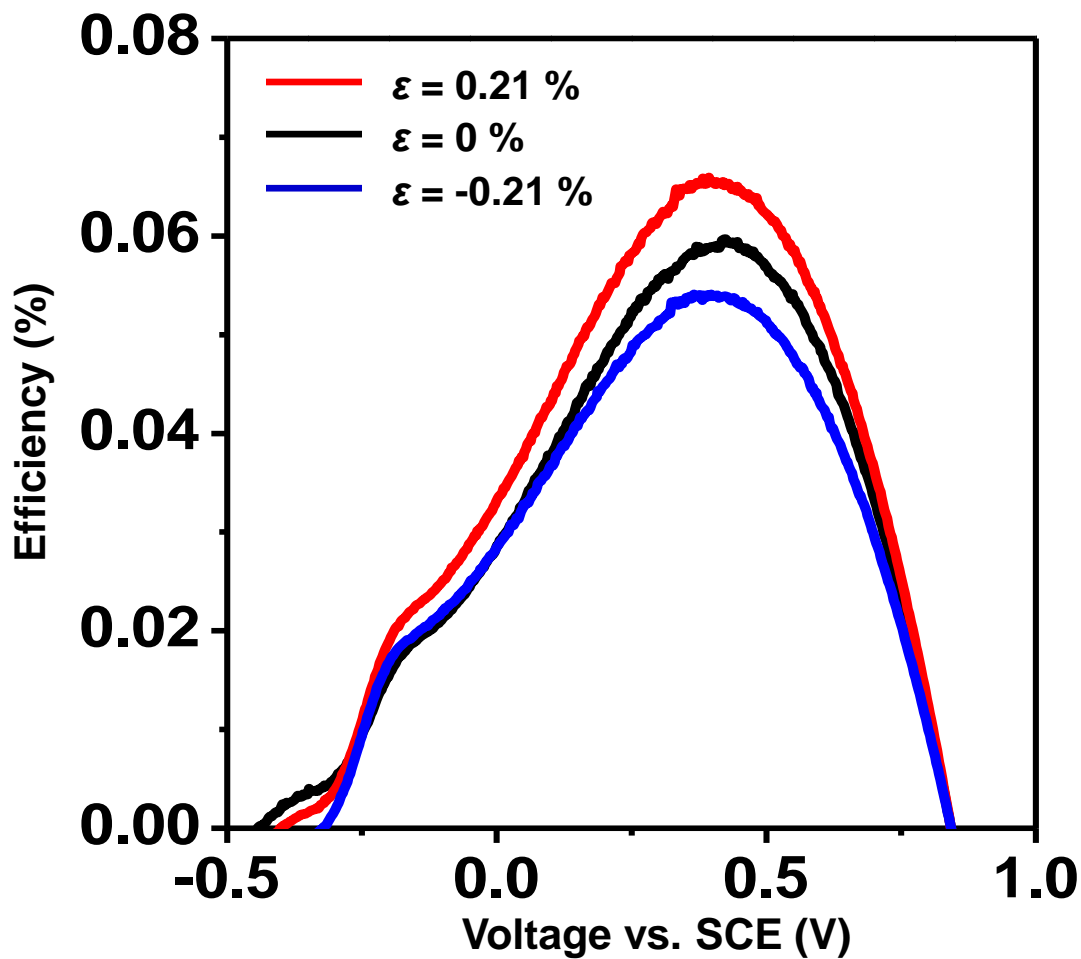


Figure S2. Efficiency versus bias potential of ZnO PZ-PEC measured under different strains. The light intensity was 100 mW cm^{-2} . When 0.21% strain was applied toward ZnO anode, the maximum efficiency increased by $\sim 10.2\%$ compared to the efficiency at zero strain. 8.5% maximum efficiency decrease was observed when -0.21% strain was applied.

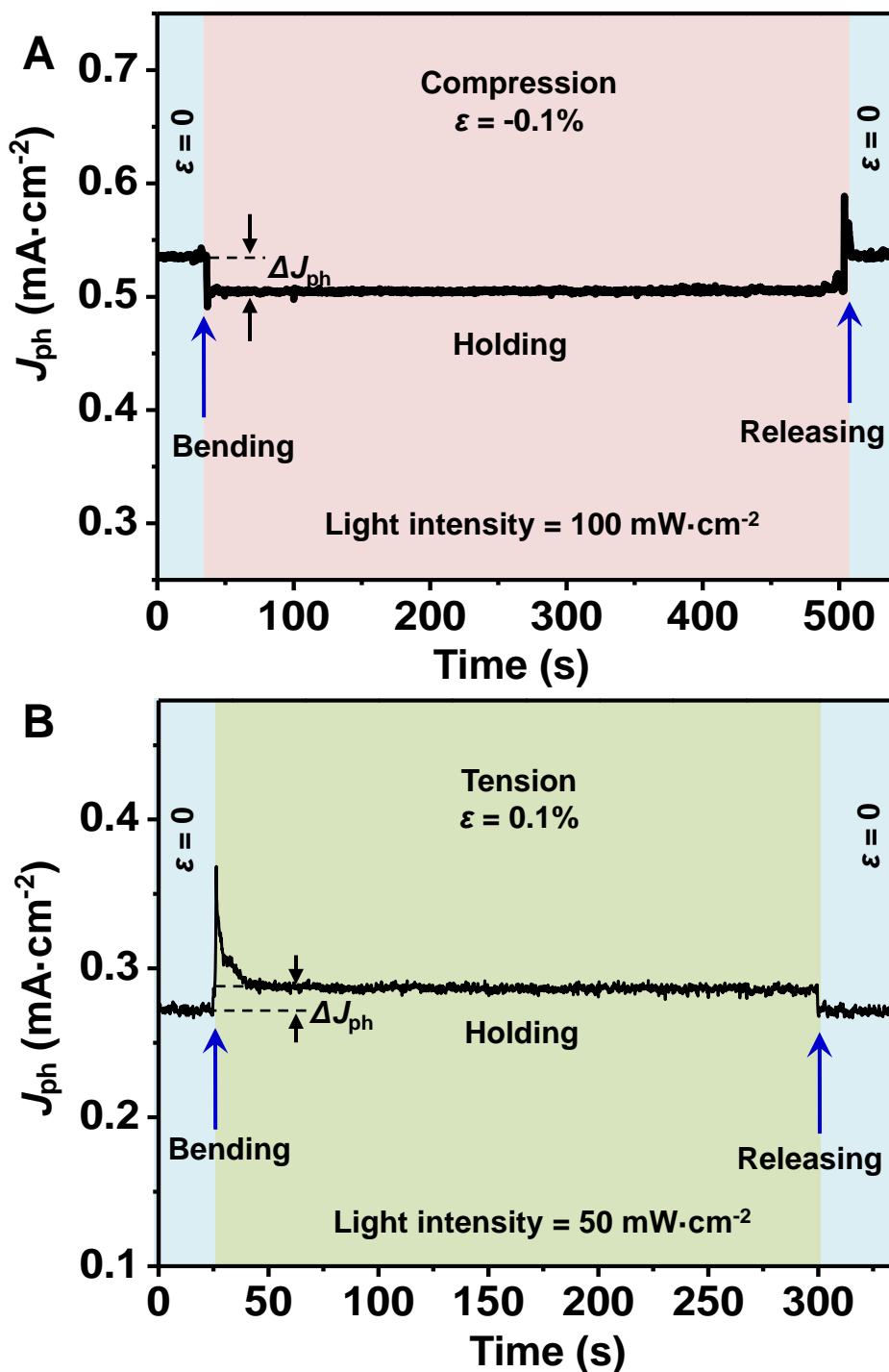


Figure S3. Stability characterization of J_{ph} variation. **A.** A constant J_{ph} reduction of $31 \mu\text{A}/\text{cm}^2$ was recorded when the PEC anode was under a constant compressive strain of -0.1% . The illumination intensity was $100 \text{ mW}/\text{cm}^2$. **B.** J_{ph} increased by $14 \mu\text{A}/\text{cm}^2$ when a tensile strain of 0.1% was applied under an illumination of $50 \text{ mW}/\text{cm}^2$.

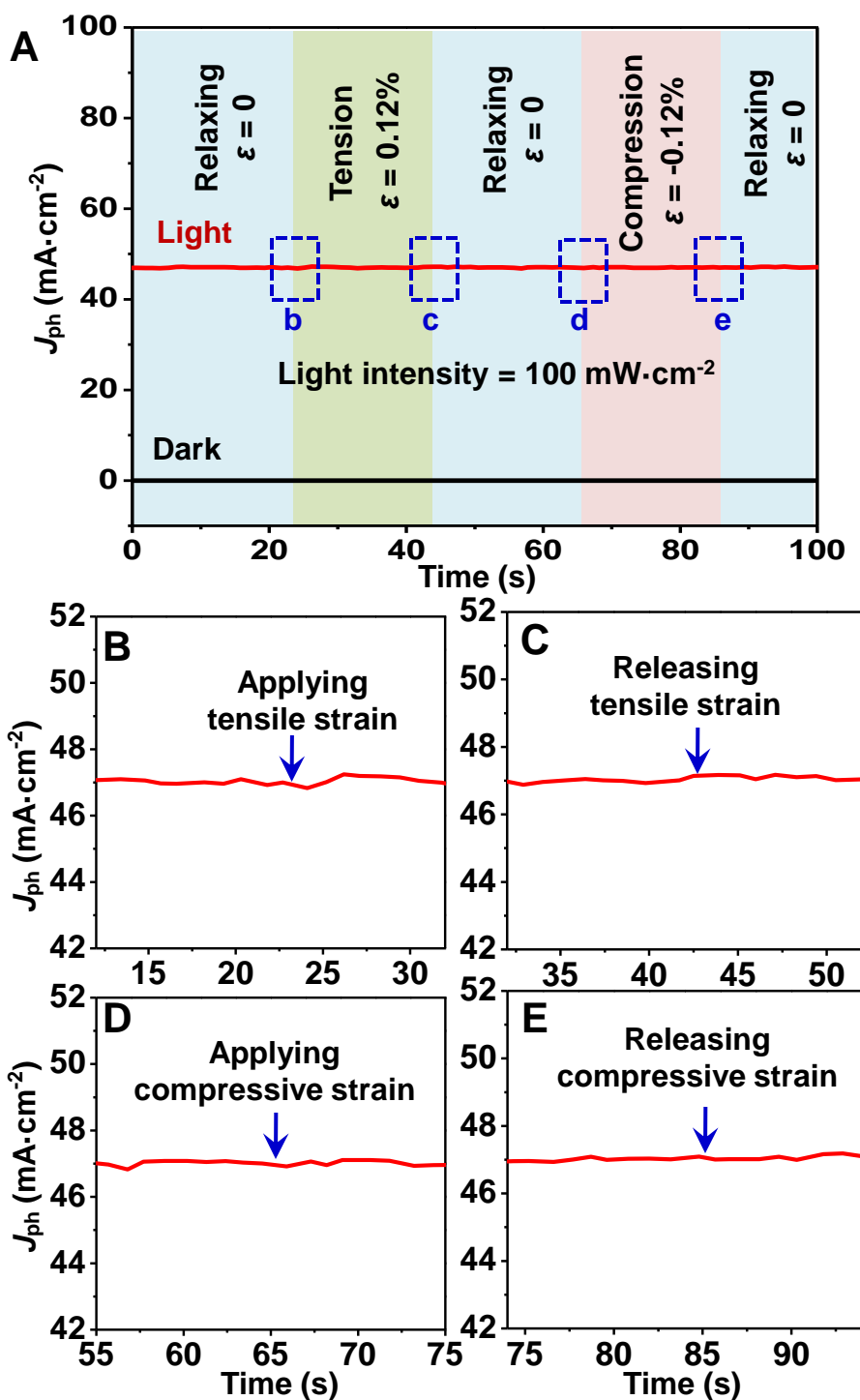


Figure S4. Control experiments on TiO_2 -based photoanode. A. J_{ph} and dark current when the TiO_2 anode was subjected to compressive and tensile strains. No noticeable current density change could be observed. B.-E. Zoom-in of J_{ph} at the moments when tensile strain was applied B. and released C. and compressive strain was applied D. and released E.

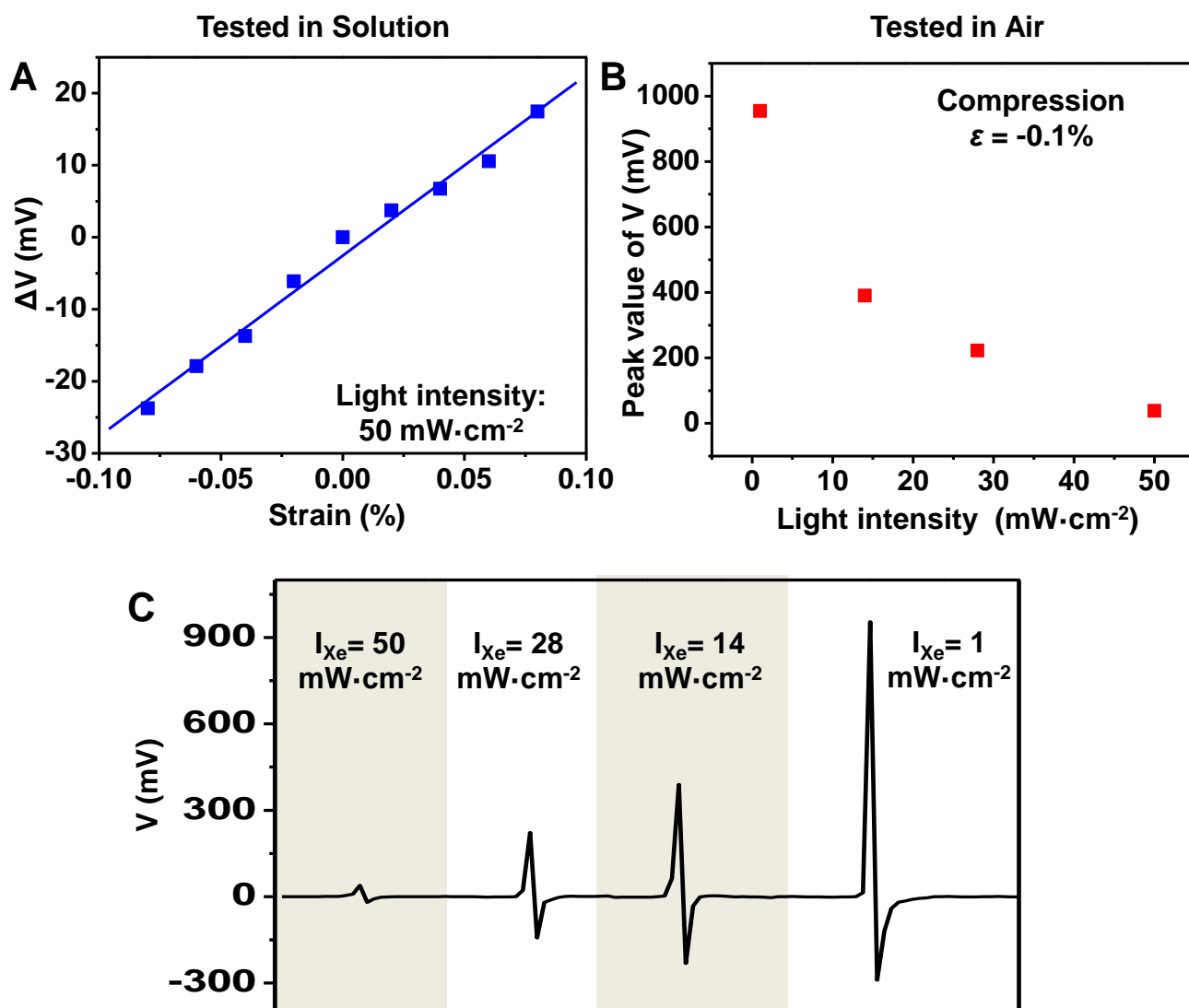


Figure S5. Piezoelectric potential measurements from strained ZnO anode. **A.** Piezoelectric potential measured from ZnO PZ-PEC inside $0.5 \text{ M K}_2\text{SO}_4$ solution. The piezoelectric potential exhibited a linear relationship with the applied strain and the light intensity was $50 \text{ mW}/\text{cm}^2$. **B.** Piezoelectric potential measured from ZnO PZ-PEC under different light intensities and the same compressive strain. Higher light intensity resulted in lower piezoelectric potential. **C.** Typical piezoelectric potential spikes recorded under different light intensities, where the compressive strain was kept the same -0.1% .

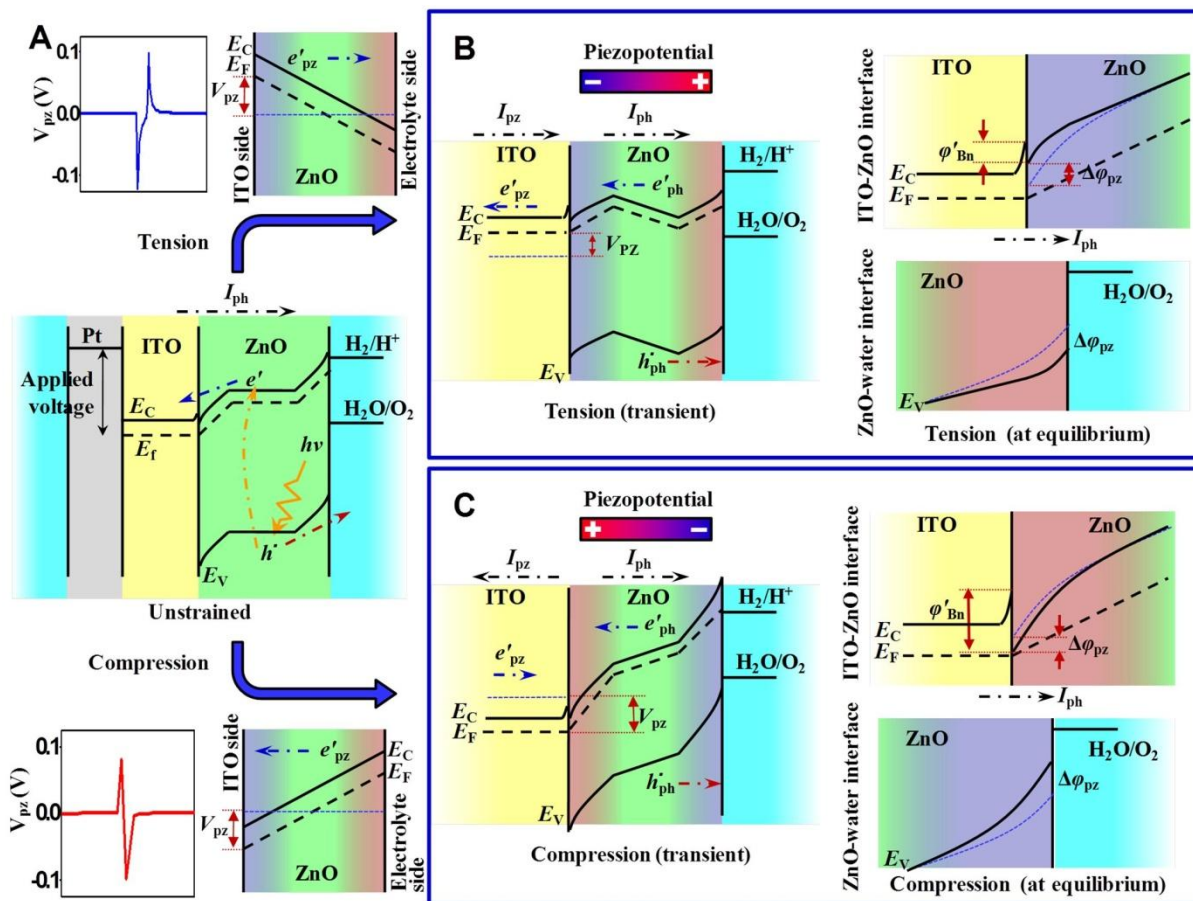


Figure S6. Band structure of the ZnO/ITO PEC anode for explaining the strain-induced photocurrent change. **A.** Middle graph: Schematic band diagram of the ZnO/ITO PEC system when an external bias is applied between working electrode (ZnO/ITO) and counter electrode (Pt gauze). No strain is applied to the ZnO anode. Top and bottom graphs show the piezoelectric potential (left graphs) and the corresponding instantaneous band tilting in ZnO (right graphs) when the ZnO film is subject to tensile and compressive strain, respectively. V_{pz} represents the maximum measurable piezoelectric potential due to straining. Band alignment of the working ZnO/ITO anode during tensile **B.** and compressive **C.** strains. Left graphs illustrate the transient band structure immediately after straining, where no charge screening is assumed to occur through the external circuit. The conduction and valence bands inside ZnO are the superposition of space charge-induced band shifting and instant polarization-induced band bending. Right graphs are the equilibrium band alignment after charge redistribution is completed, while ZnO is still under strain for the ITO/ZnO (top) and ZnO/electrolyte (bottom) interfaces. The depolarization field at the heterogeneous interface shifts the bands from their original position (dashed blue curves) to a new position (solid black lines), and thus changes the interface barrier height.