

SUPPORTING INFORMATION

A Sustainable Light-Chargeable Two-Electrode Energy Storage System based on Aqueous Sodium-Ion Photo-Intercalation

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Experimental Section

CdS-(TiO₂)-WO₃ electrode fabrication

Similar to our previous work,¹ the WO₃ film was first fabricated by 10 times repeated 20s spin coating of 0.25 M WCl₆ (99.9 %, Sigma Aldrich) in isopropanol solution on FTO glass which was heated for 5 mins at 250 °C on a hot plate after each coating. The as-deposited film was then annealed at 500 °C for 30 min in air, followed by 40 mM TiCl₄ aqueous solution treatment for 40 min at 80 °C as done in dye-sensitized photoanode fabrication. The TiO₂ decorated WO₃ film was again annealed at 500 °C. Subsequently, CdS as light absorber/sensitizer was deposited by chemical bath deposition (CBD) at 65 °C using 1.5 mM CdSO₄, 3.75 ammonia (1.85M), and thiourea (75 mM) to prepare the reacting aqueous bath solution.

Cu₂S counter electrode fabrication

To prepare Cu₂S counter electrode, brass foil (Cu-Zn alloy, Model: Ultra-Machinable 360 Brass, Thickness: ~3 mm) purchased from McMaster-Carr, was at first immersed in boiling concentrated HCl solution (~36 %) for 30 min and then washed and dried. **This treatment was to electrochemically etch away the Zn to expose pure Cu on the surface for the next step reaction.** Then a polysulfide aqueous solution was prepared by dissolving 1 M Na₂S and 1 M S in DI water. After that, the brass foil with partially etched Zn on the surface was dipped into the polysulfide solution for 5 min to rapidly form black Cu₂S on the surface of brass.

Materials Characterization

Thermo Scientific K-Alpha X-Ray Photoelectron Spectroscopy (XPS) was used for surface analysis; (C 1s peak at binding energy of 285 eV was used for charge correction). Hitachi SU-8230 Field Emission-STEM (FE-STEM) with Oxford EBSD and INCA EDS was used for high resolution SEM secondary electron and backscatter electron images capturing and EDS mapping. Grazing angle XRD was performed by a D8 Discover Bruker copper source X-ray diffractometer, **whose goniometer has radius of 200 mm, at room temperature, with monochromated CuK α ($\lambda = 1.54 \text{ \AA}$) at glancing angle starting at 0.5°, step size of 0.05 (2 θ /s). Measurements were taken under beam-acceleration conditions of 40 kV/35 mA.**

Electrochemical Tests

The photoelectrochemical tests were firstly performed with 2 M Na₂SO₃ and 0.2M Na₂S dissolved in water as electrolyte, platinum foil (99.9 %, Sigma Aldrich) was used as counter electrode. Later 0.2 M Na₂S in water was used directly as electrolyte with Cu₂S as counter electrode instead of Pt. Ag/AgCl (in saturated KCl) was used as reference electrode to monitor the potential of working electrode. All electrochemical tests were performed using a VSP-potentiostat system (BioLogic). A small area class-BBA solar simulator (PV Measurements Inc.) was used for photo rechargeable

battery light charging test. A secondary silicon reference cell was used to calibrate the illumination light power at the testing position to be 100 mW/cm^2 (1 sun). The reduced light power to 0.5 Sun and 0.25 Sun was realized by applying optical filters (Thorlabs, Inc.). An IPCE/EQE system from PVM Inc. was used to provide monochromatic light for transmittance and EQE measurement. All tests were performed in ambient atmosphere.

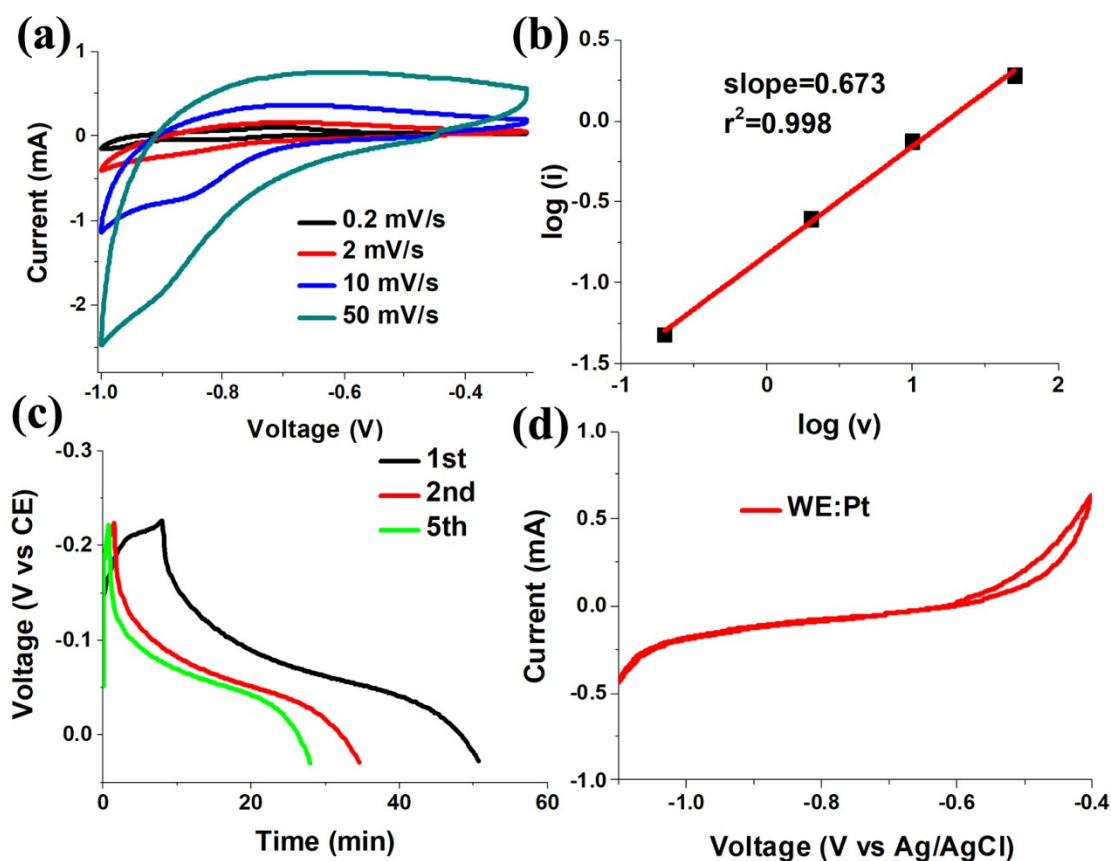


Figure S1 a) Cyclic voltammograms of $\text{WO}_3\text{-TiO}_2\text{-CdS}$ working electrode (WE) at various sweep rates in $2 \text{ M Na}_2\text{SO}_3 + 0.2 \text{ M Na}_2\text{S}$ aqueous electrolyte (the voltage is for the WE vs. Ag/AgCl reference electrode, RE); b) variation of the peak current as a function of sweep rate; c) voltage profiles of light charge – dark discharge at 10 uA with fixed voltage window, here voltages were WE vs Pt counter electrode (CE); d) cyclic voltammograms of Pt at 1 mV/s sweep rate.

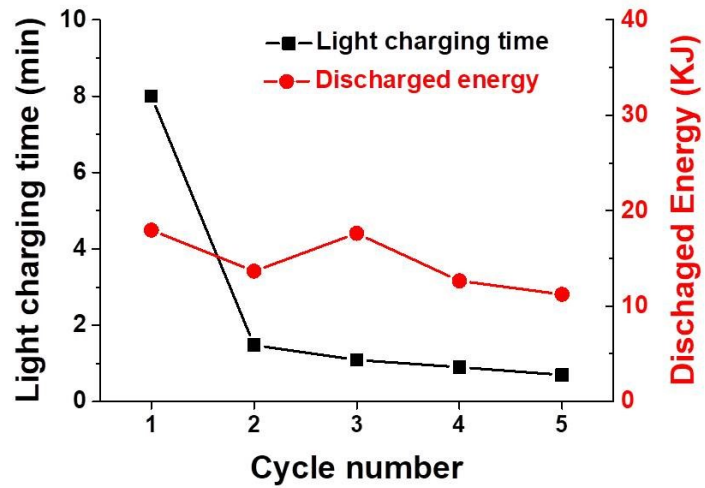


Figure S2 The light charging time and discharged energy extracted for the system operating at controlled voltage window (-0.85 V ~ -0.6 V).

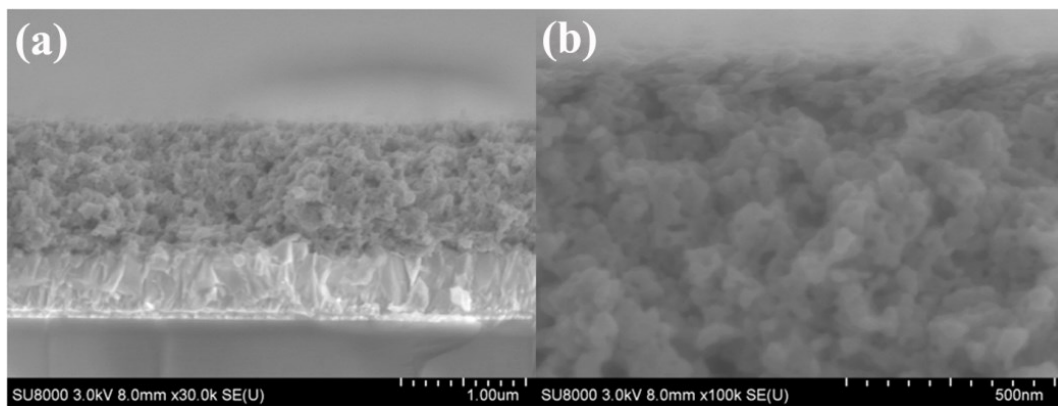


Figure S3 SEM cross-sectional images of WO₃ (TiO₂ coated) on FTO.

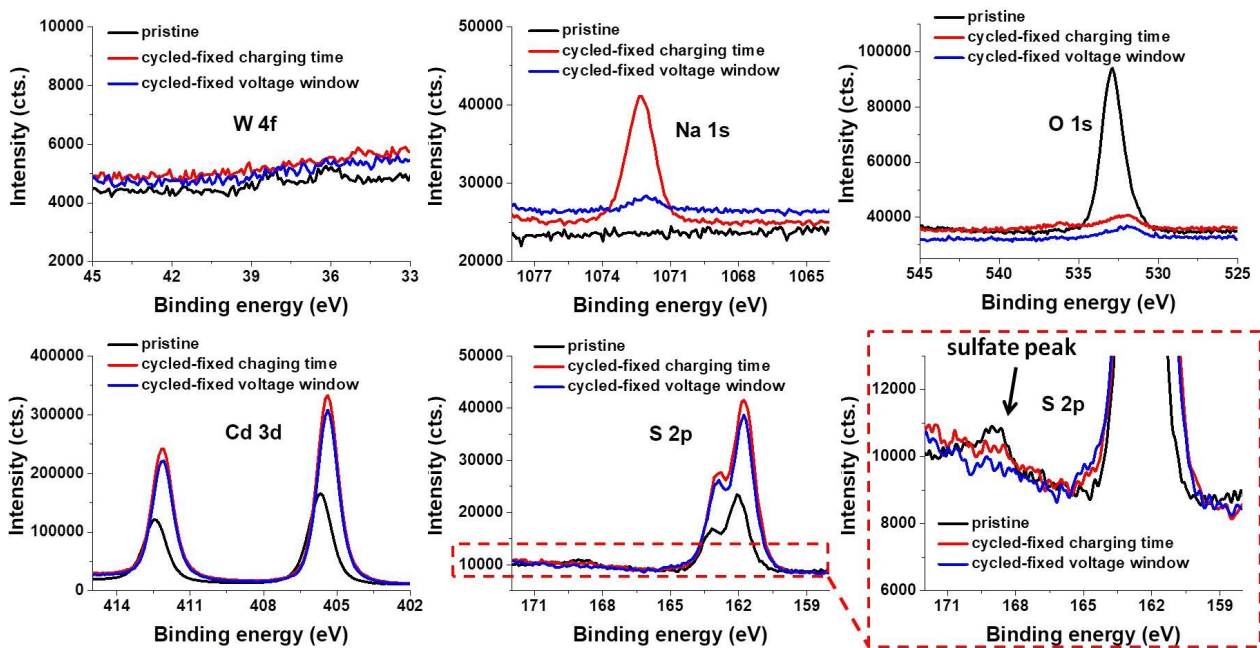


Figure S4 XPS spectra of pristine, fixed photocharging time-cycled, and fixed voltage window-cycled $\text{WO}_3\text{-(TiO}_2\text{)-CdS}$ electrodes.

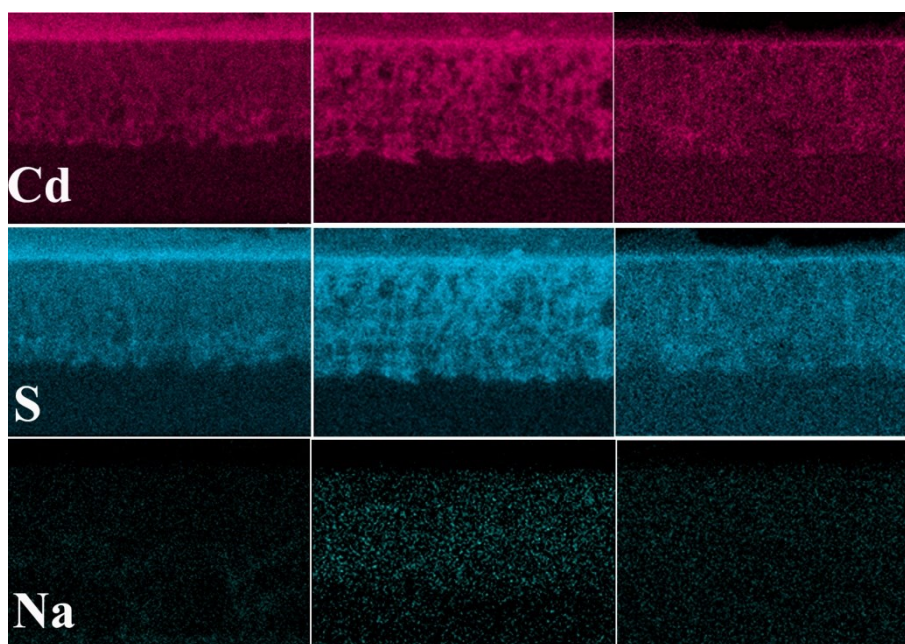


Figure S5 EDS maps of Cd, S, and Na in $\text{WO}_3\text{-(TiO}_2\text{)-CdS}$ pristine (left column), fixed light charging time cycled (middle column), and fixed voltage window cycled electrodes (right column).

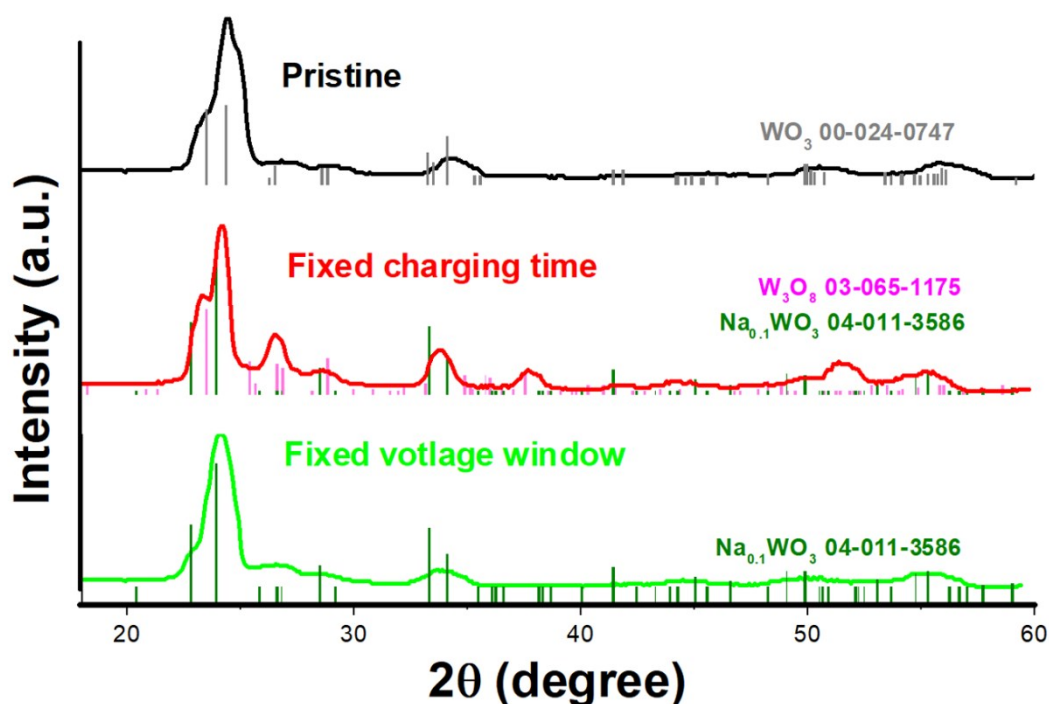


Figure S6 XRD characterization of the pristine photoelectrode $\text{WO}_3\text{-(TiO}_2\text{)-CdS}$ (black); XRD of the 5th-cycled electrode with photo-charging for 10 min (red, fixed charging time); and the XRD of the 5th-cycled electrode with photo-charging to -0.85 V (green, fixed voltage window). The reference patterns include monoclinic WO_3 (00-024-0747), orthorhombic W_3O_8 (03-065-1175), and tetragonal $\text{Na}_{0.1}\text{WO}_3$ (04-011-3586).

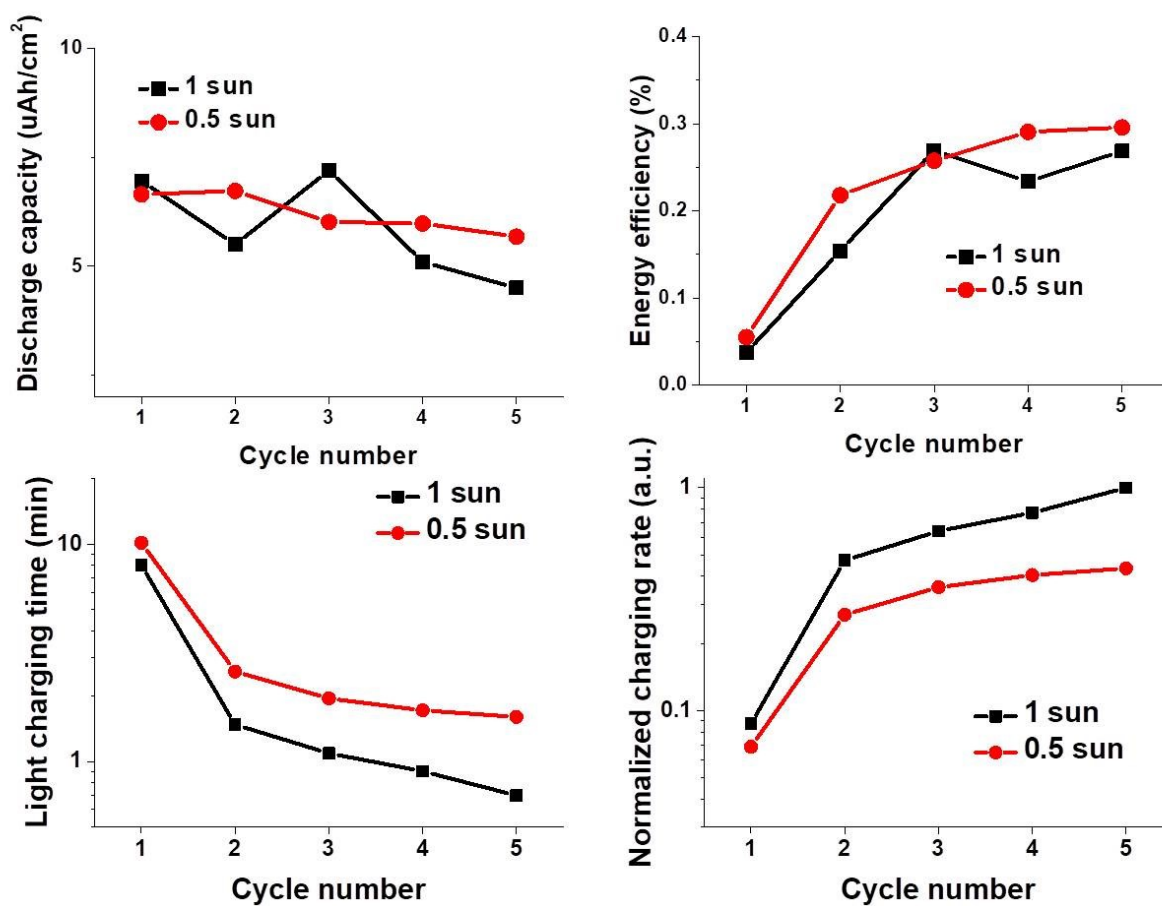


Figure S7 Variations of discharge capacity, energy efficiency, light charging time, and normalized charging rate with cycle number after being charged at different light intensity within fixed voltage window and discharged at 10 μ A in dark.

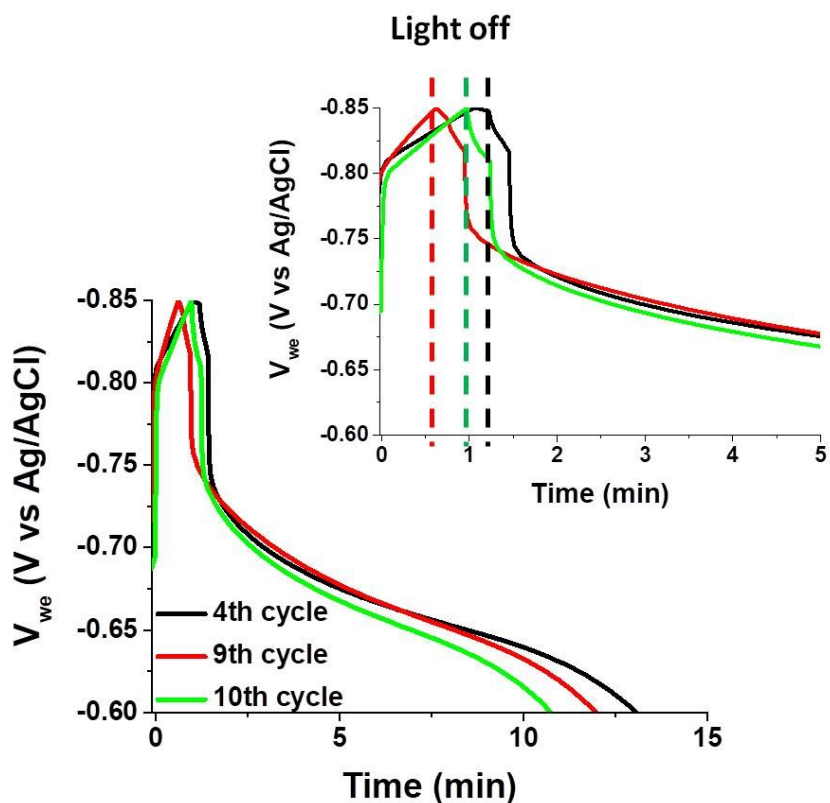


Figure S8 Voltage profiles (vs Ag/AgCl) of 4th, 9th and 10th cycle (at the rate of 20 μ A) of working electrode (WE) operating at varying rates (fixed voltage window at 0.5 Sun).

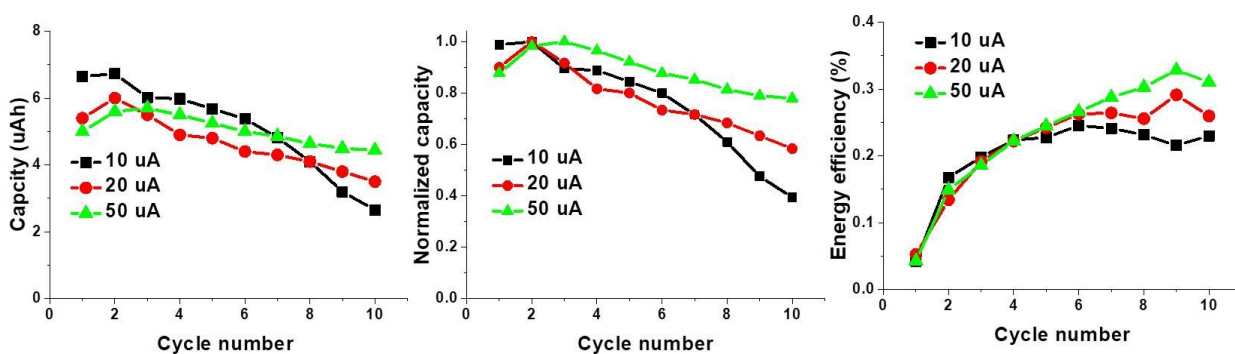


Figure S9 The variation of discharge capacity, normalized capacity, and energy efficiency of electrodes discharging at different rates cycled for 10 times (fixed voltage window at 0.5 Sun).

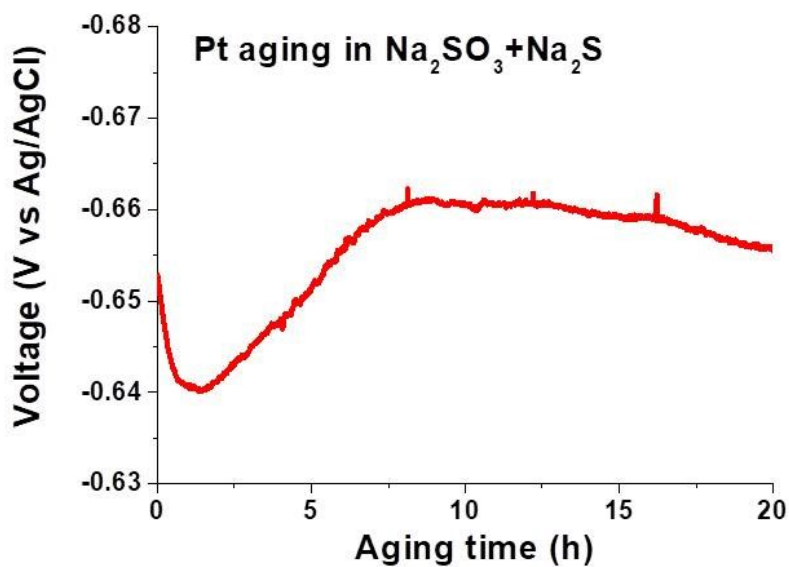


Figure S10 Potential variation of a Pt foil exposed in the sulfite/sulfide testing electrolyte as function of time.

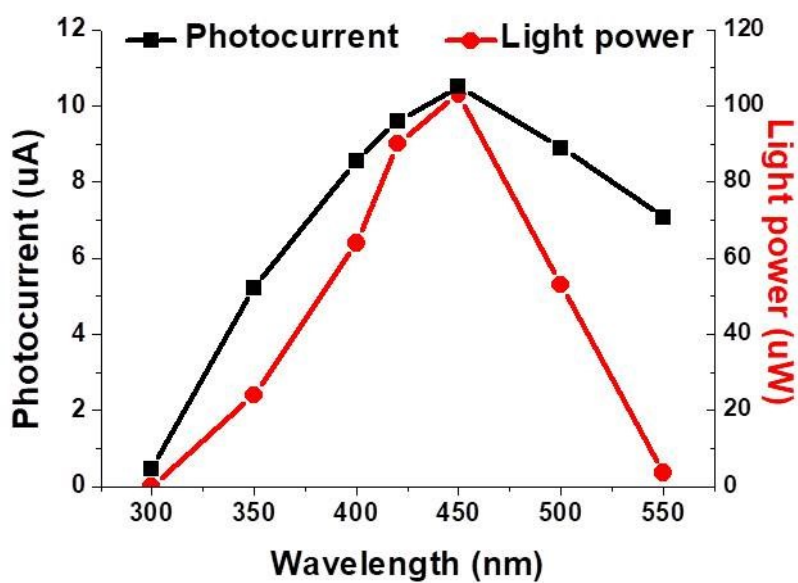


Figure S11 Photocurrent output of WO₃-(TiO₂)-CdS photo-electrode under short circuit condition and illumination at variable applied monochromatic light power.

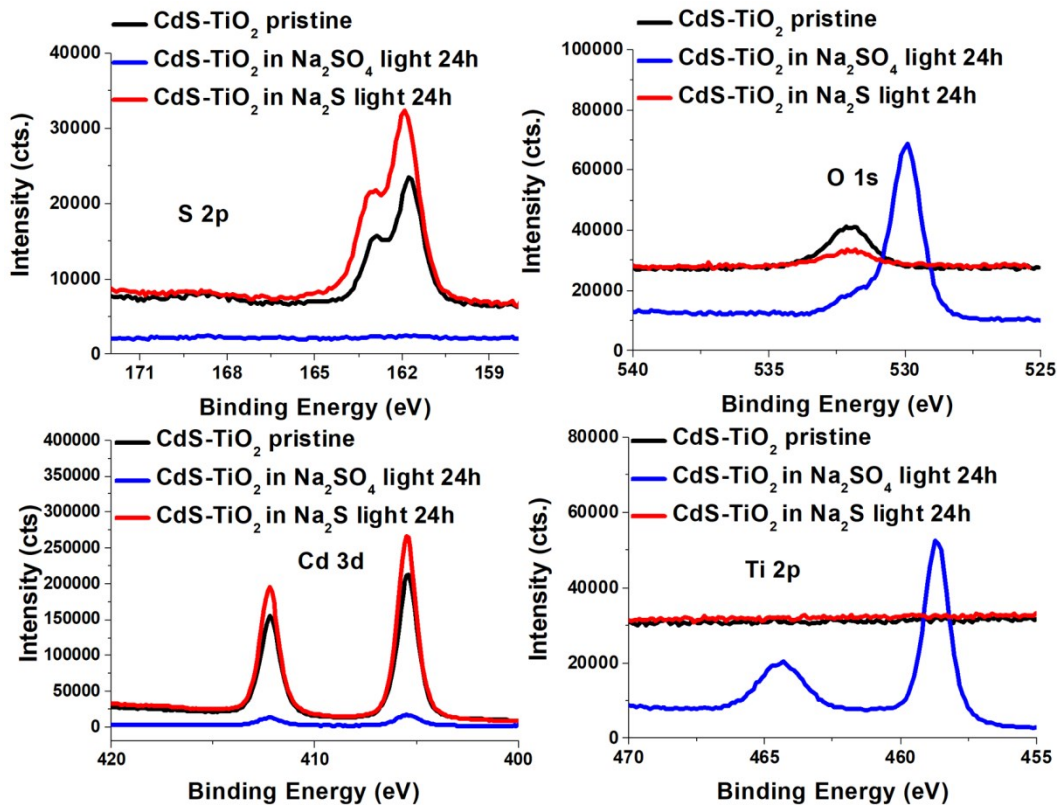


Figure S12 XPS spectra of CdS on TiO₂ thin layer (CdS-TiO₂) that were being light soaked for 24 h in either 0.2 M Na₂SO₄ or 0.2 M Na₂S.

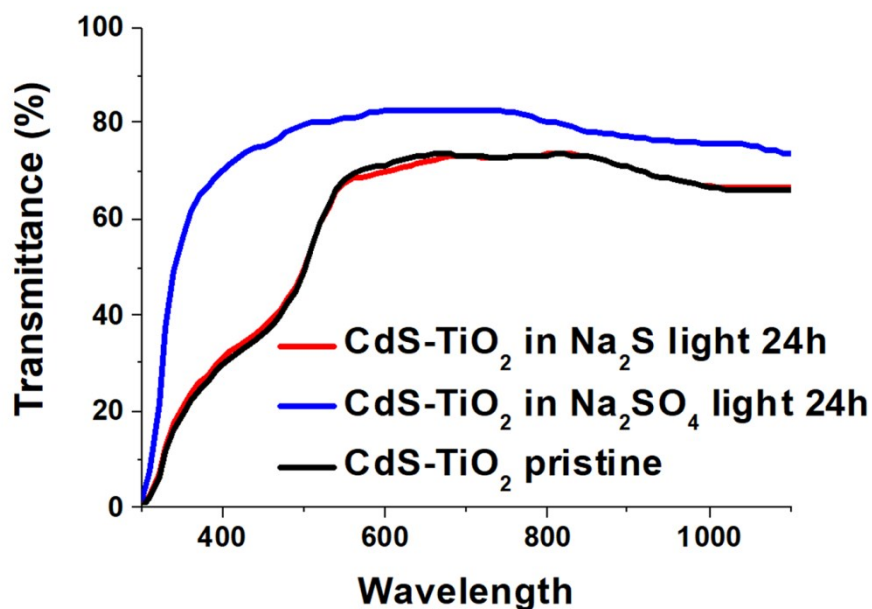


Figure S13 Transmittance of CdS on TiO₂ thin layer (CdS-TiO₂) that was light soaked for 24 h in either 0.2 M Na₂SO₄ or 0.2 M Na₂S.

Reference

1. Wang, Z.; Chiu, H.-C.; Paoella, A.; Zaghbi, K.; Demopoulos, G., Lithium Photo-Intercalation of

CdS-Sensitized WO₃ Anode for Energy Storage and Photoelectrochromic Applications.
ChemSusChem **2019**, *12*, 2220-2230.