Supporting Information

Linear PDI-based Conjugated Polymers with Oriented Charge Transport Driving Photocatalytic Water Oxidation

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Chemicals: All the materials were purchased from Aladdin, Macklin or Adamas and used without further purification. 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and imidazole were purchased from Aladdin. p, p'-diaminobiphenyl (CB) was purchased from Macklin. 3,7-Diaminodiphenylene sulfone (CS) and zinc acetate ($Zn(CH_3COO)_2$) were purchased from Adamas.

***Synthesis of PT-CB Polymer*:** PT-CB was synthesized via imidazole solvent method following the previous report. 78.4 mg PTCDA, 36.8 mg CB, 36.7 mg $Zn(CH_3COO)_2$ and 2g of imidazole as solvent were charged into a 10 mL Pyrex tube. After replaced air by nitrogen for three times to build nitrogen atmosphere, the tube was sealed then heated to 140 ℃ and keep stirring for 24 hours to form product. After cooling, the product was dispersed in 1 M HCl and stirred for 1h and then use vacuum filtration to remove liquid and washed solid with distilled water until the pH of filtrate to 7. Subsequently, the precipitate was further washed by hot saturated potassium carbonate solution and distilled water for several times. Finally, washing with DMSO and dried under vacuum at 60 ℃ overnight, resulting in a dull red powder.

***Synthesis of PT-CS Polymer*:** PT-CS was synthesized via imidazole solvent method following the previous report. 78.4 mg PTCDA, 49.2 mg CS, 36.7 mg $Zn(CH_3COO)_2$ and 2g of imidazole as solvent were charged into a 10 mL Pyrex tube. After replaced air by nitrogen for three times to build nitrogen atmosphere, the tube was sealed then heated to 140 ℃ and keep stirring for 24 hours to form product. After cooling, the product was dispersed in 1 M HCl and stirred for 1h and then use vacuum filtration to remove liquid and washed solid with distilled water until the pH of filtrate to 7. Subsequently, the precipitate was further washed by hot saturated potassium carbonate solution and distilled water for several times. Finally, washing with DMSO and dried under vacuum at 60 ℃ overnight, resulting in a dull red powder.

Characterization: The products XRD were characterized using RIGAKU SmartLab. FT-IR spectrum were collect used VERTEX70 spectrometer. ^{13}C NMR was performed on an AVANCE III spectrometer. SEM was conducted by SU8010 at 5 kV. TEM images were acquired from Talos-F200X. XPS spectra was collected using ESCALAB 250xi (Thermo Scientific) with Al Kα radiation. UV-vis was got from Lambda 950 with $BaSO_4$ as the reference.

Photocurrent, Electrochemical Impedance Spectroscopy (EIS) and Mott-Schottky(MS) measurements: 5 mg of catalyst was dispersed in 900 mL ethanol and 100 μL of 5 % Nafion

solution sonication to form slurry. The slurry was applied to an FTO glass substrate and air dried. Measurements were performed on CHI 600E electrochemical workstation using three-electrode system the FTO glass served as the photoelectrode, Pt as the counter, Ag/AgCl as the reference electrode and 0.5 M Na_2SO_4 as electrolyte.

DFT calculation were performed using the Materials Studio software version 2020. The Perdew-Burke-Ernzerhoff (PBE) functional was used to treat exchange-correlation effects within the generalized gradient approximation (GGA) level. A Monkhorst-Pack Gamma-centered scheme to sample the Brillouin zone was employed with 48 × 86 × 50 customized K points. For the band structure calculations, the high-symmetry K-points are G (0, 0, 0), Z (0, 0, 1/2), T (-1/2, 0, 1/2), Y (-.05, 0, 0), S (-1/2, 1/2, 0), X (0, 1/2, 0), U (0, 1/2, 1/2) and R (-1/2, 1/2, 1/2).

Photocatalytic oxygen evolution experiment. The experiment of photocatalytic oxygen evolution was carried out by an online photocatalytic system (LabsolarI-6A, Beijing Perfectlight Technology Co., Ltd). Initially, 5 mg photocatalyst and 850 mg $AgNO_3$ (sacrificial agent) were first disperse in 100 mL water to create a reaction solution. Then, it was moved into a photo-reactor. After removing all dissolved air from the system through degassing and filling Ar, the reaction solution was exposed to a Xe lamp (300W power) with magnetic stirring in Ar. To achieve simulated visible light irradiation, a 420 nm cut-off filter was employed to block ultraviolet light. The reaction solution temperature was keep at 10 °C using circulating cooling water. Finally, the produced oxygen was measured online using Gas Phase Chromatograph (GC).

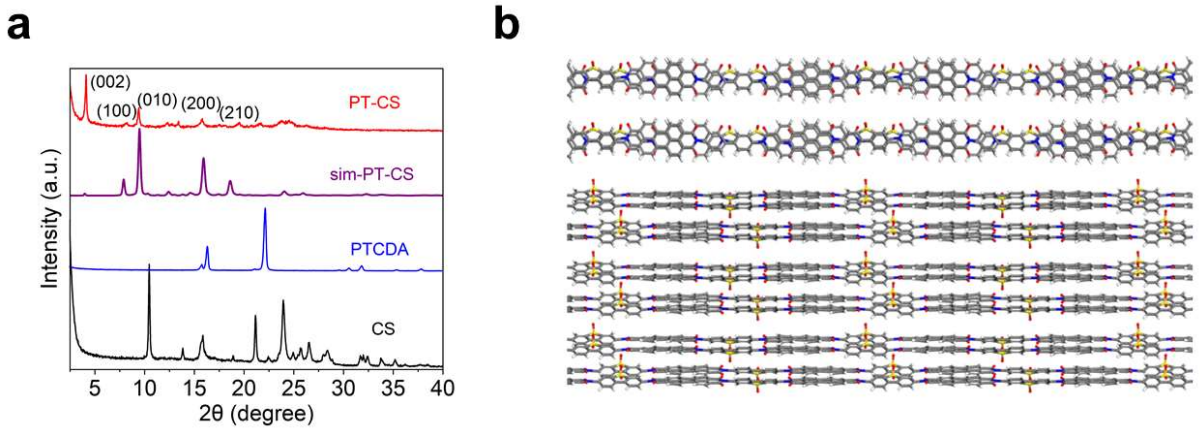

Figure S1. (a) PXRD patterns of PT-CS and (b) views of the PT-CB structure.

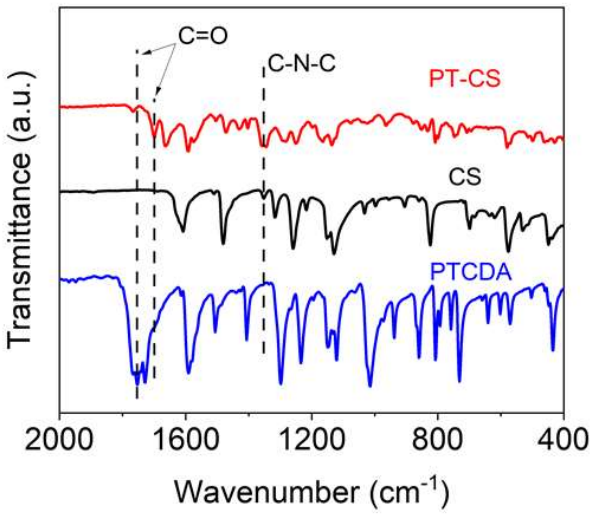

Figure S2. FT-IR spectra of PT-CS.

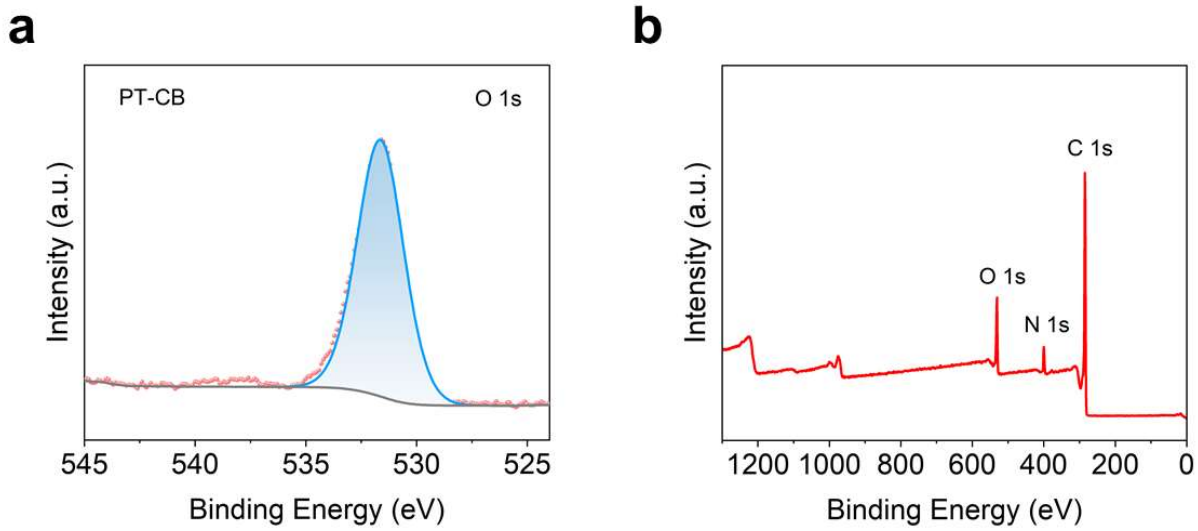

Figure S3. XPS spectra of PT-CB.

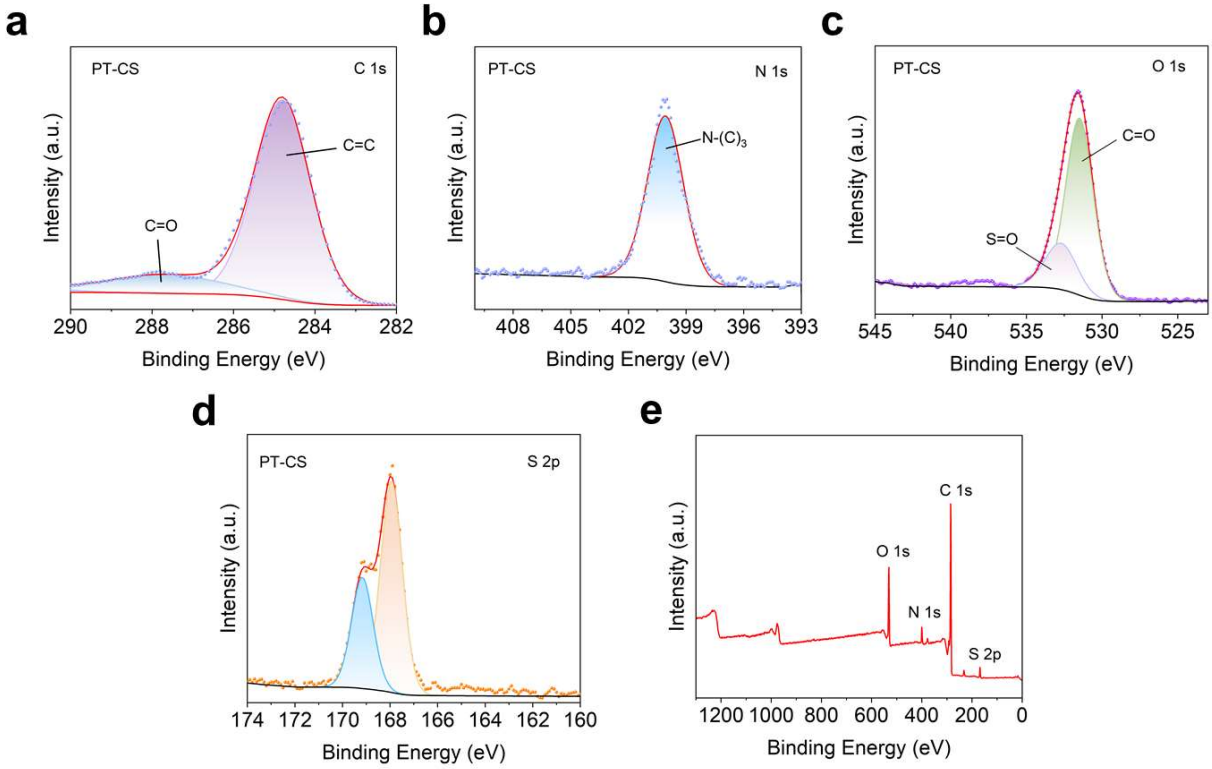

Figure S4. XPS spectra of PT-CS.

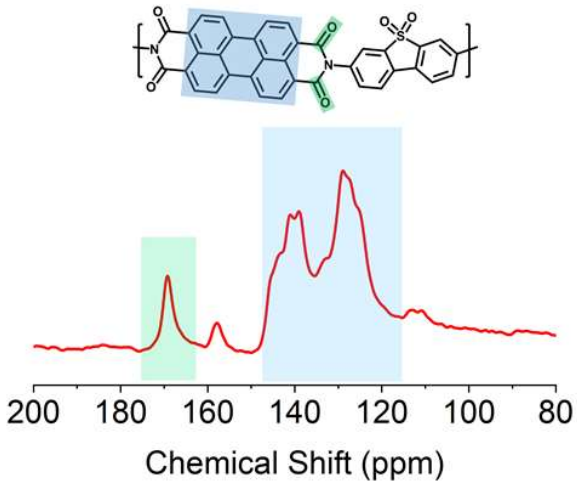

Figure S5. Solid-state ^{13}C NMR spectra of PT-CS.

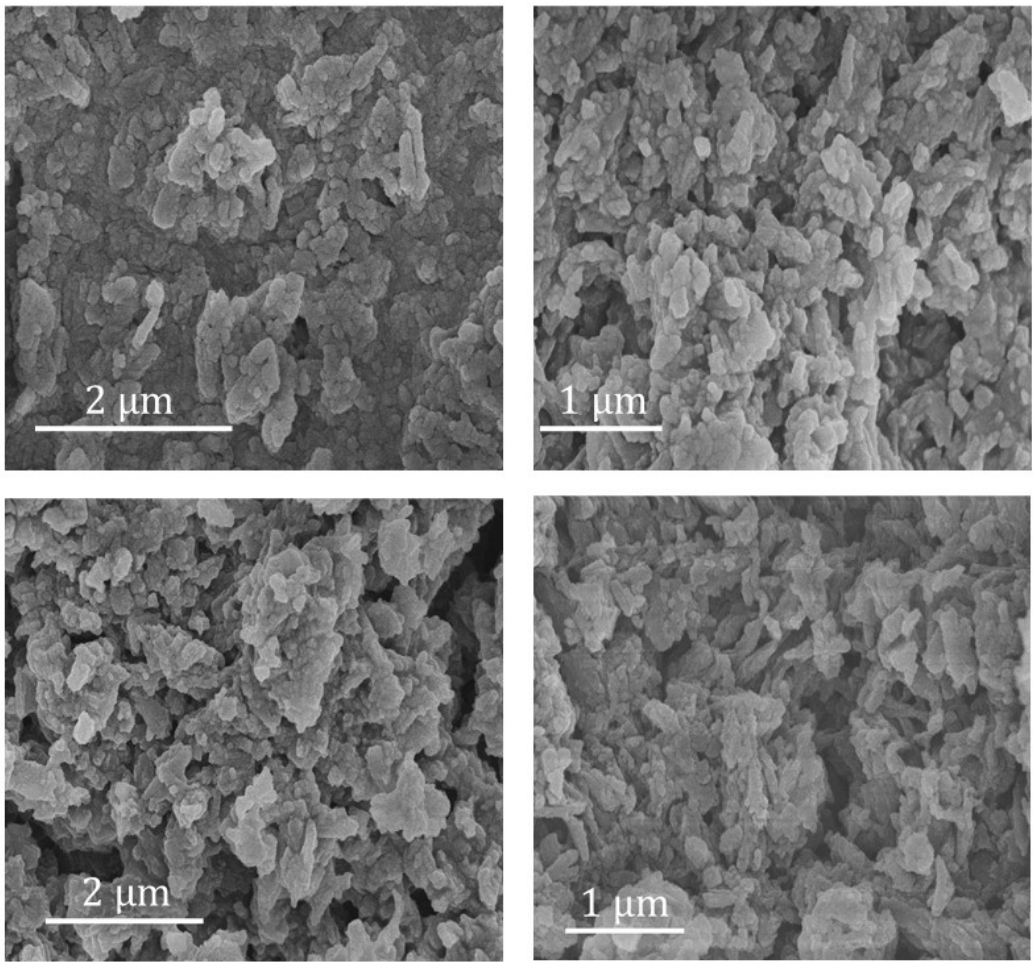

Figure S6. SEM image of PT-CB.

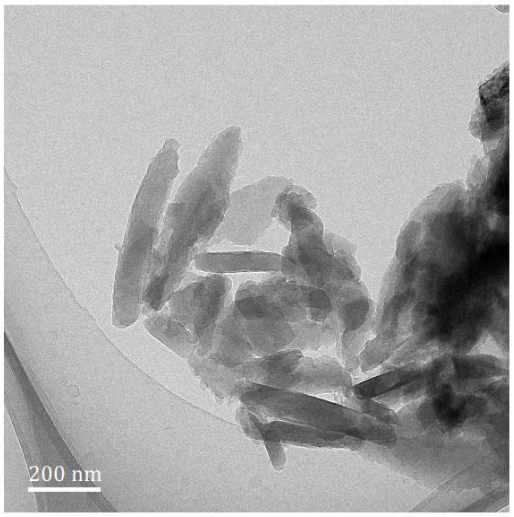

Figure S7. TEM image of PT-CB.

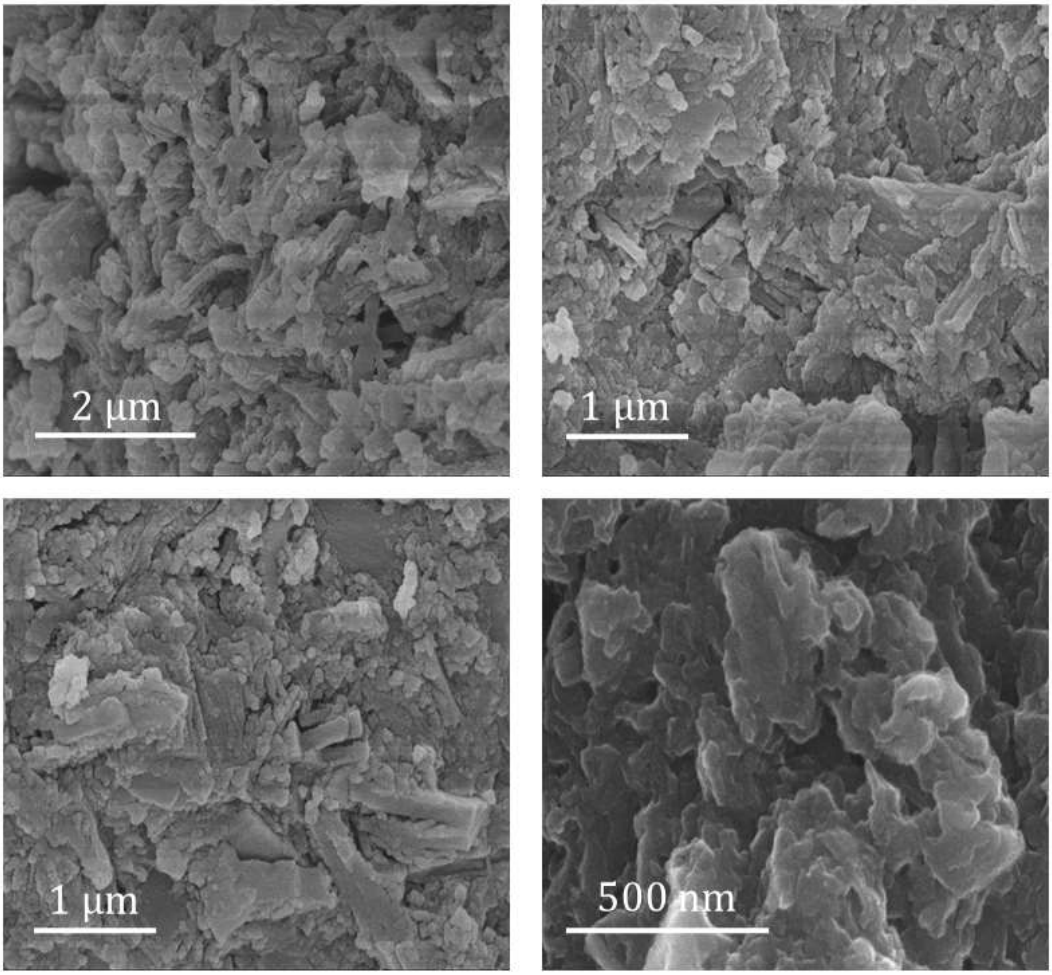

Figure S8. SEM image of PT-CS.

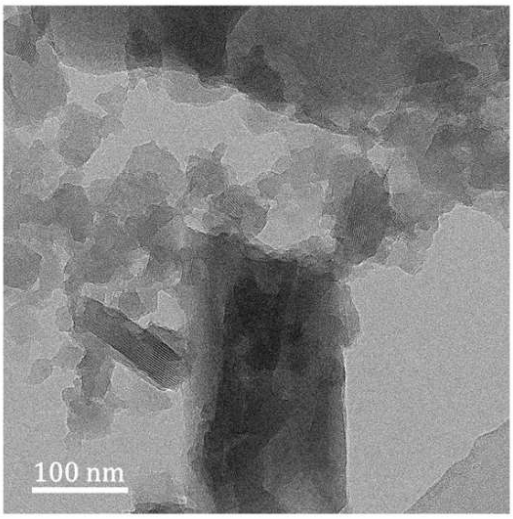

Figure S9. TEM image of PT-CS.

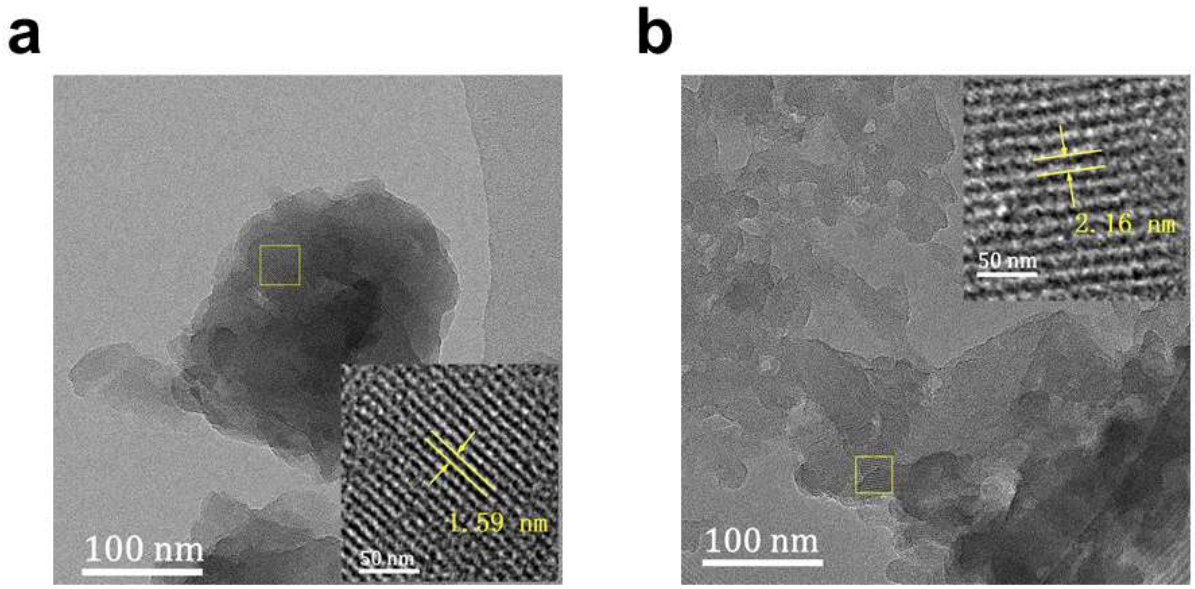

Figure S10. TEM image of (a) PT-CB and (b) PT-CS.

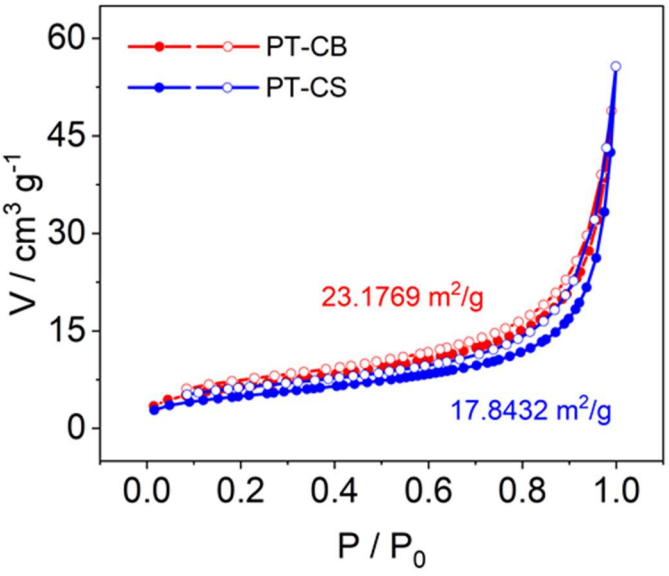

Figure S11. N_2 adsorption isotherms of PT-CB and PT-CS.

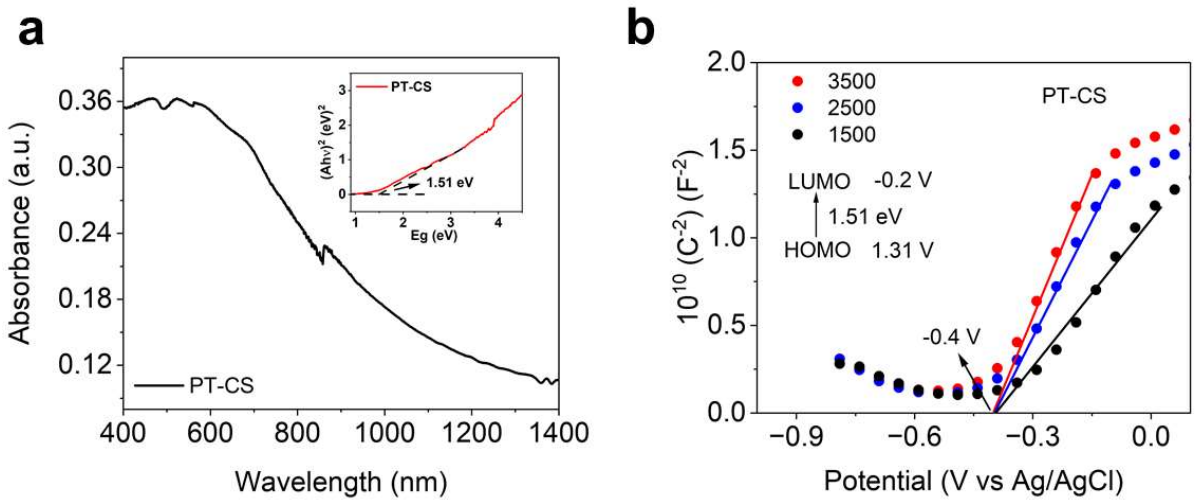

Figure S12. (a) UV–vis DRS and (b) Mott–Schottky plots of PT-CS.

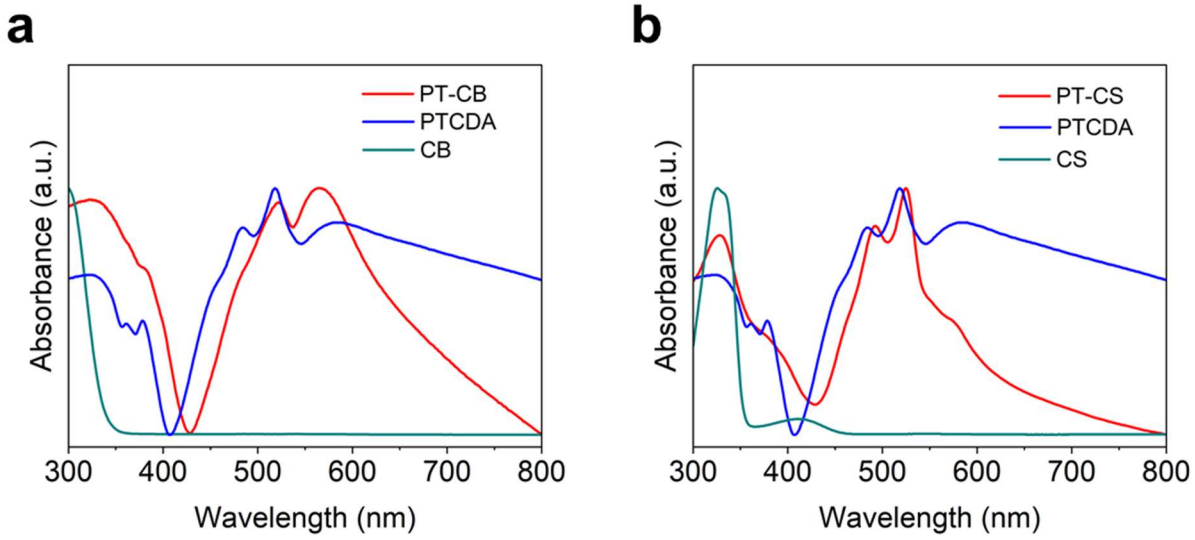

Figure S13. UV-vis absorption spectroscopy of (a) PT-CB and (b) PT-CS.

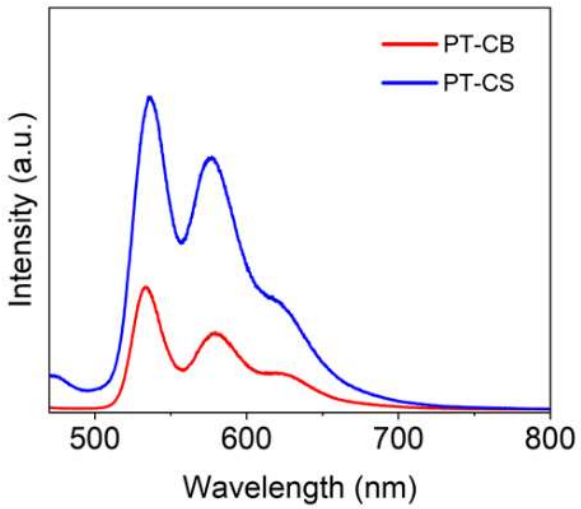

Figure S14. PL spectra of PT-CB and PT-CS.

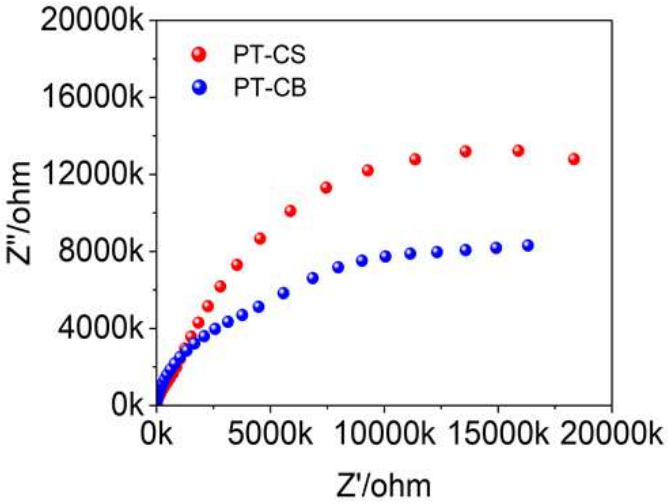

Figure S15. Nyquist plot of EIS of PT-CS and PT-CB.

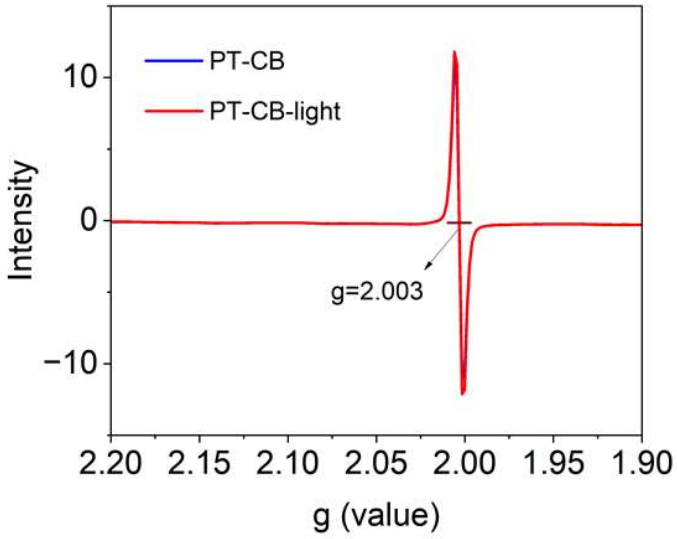

Figure S16. The EPR spectra of PT-CB under dark and light irradiation.

Figure S17. Photograph of the photocatalytic online analytical system (LabsolarI-6A, Beijing Perfectlight Technology Co., Ltd).

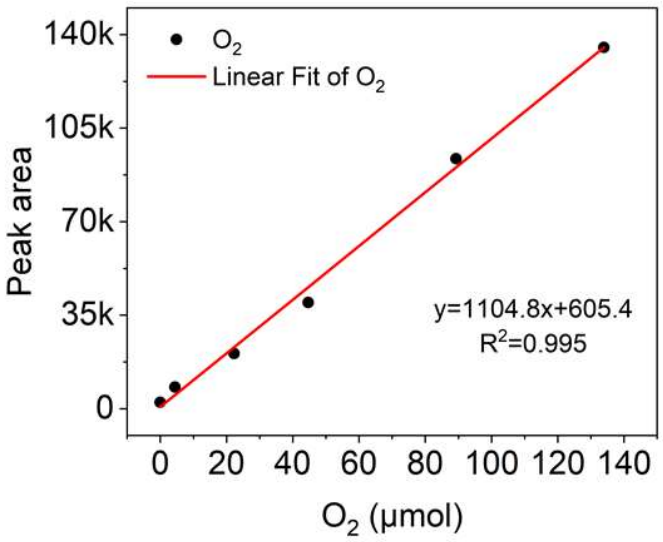

Figure S18. The calibrated standard curve of O_2 in gas chromatograph with TCD.

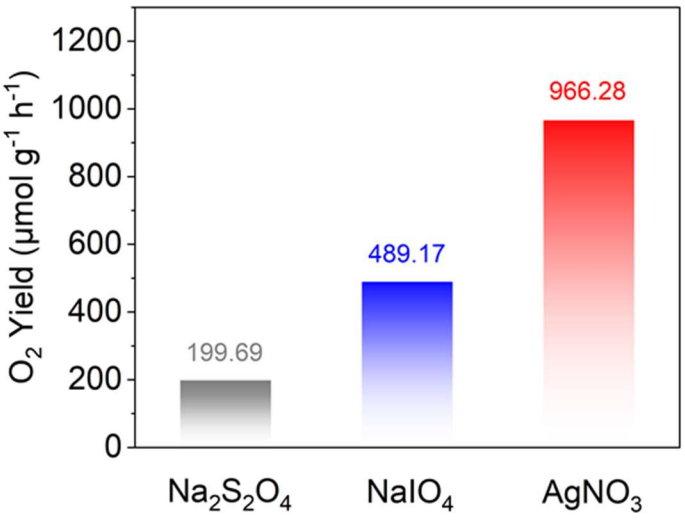

Figure S19. Oxygen evolution rates under different sacrificial agent conditions.

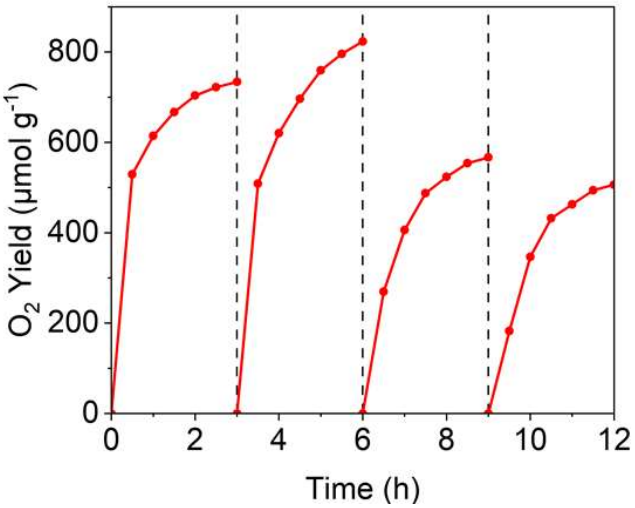

Figure S20. Cycling stability of PT-CB.

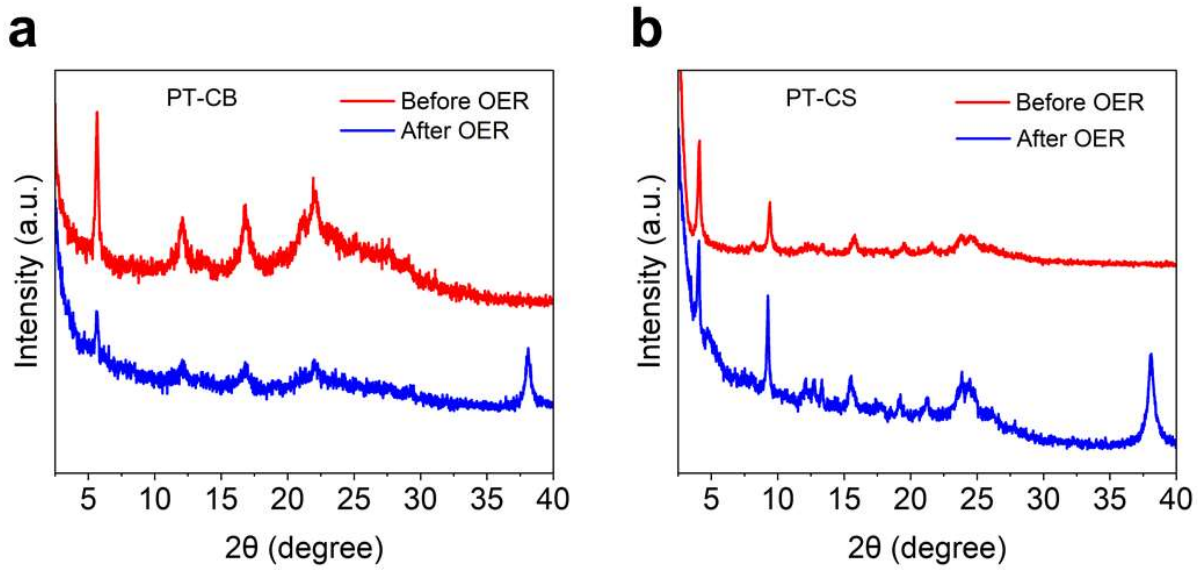

Figure S21. XRD of (a) PT-CB and (b) PT-CS before and after photocatalytic OER performance.

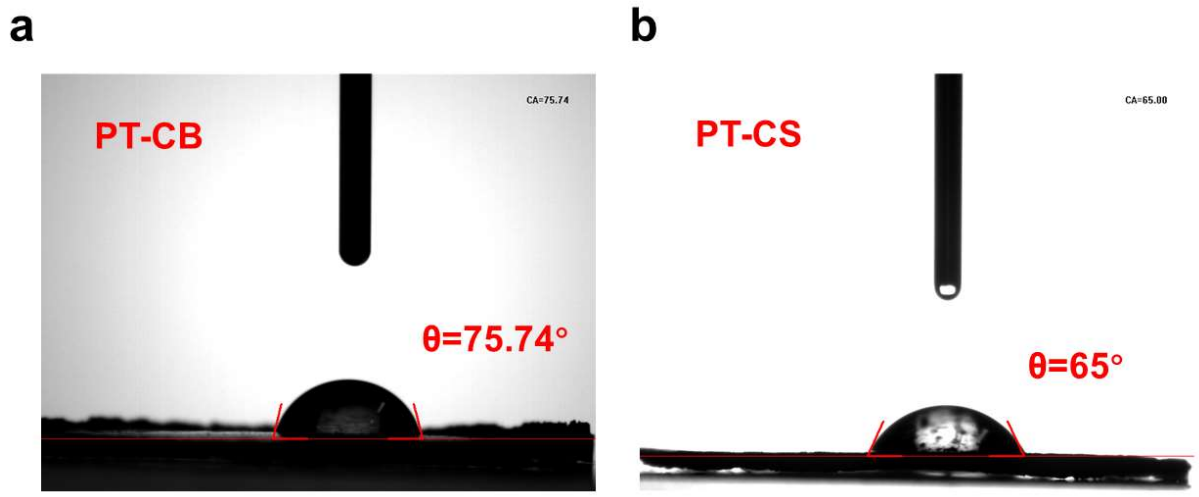

Figure S22. Contact angles of water on thin films of (a) PT-CB and (b) PT-CS.

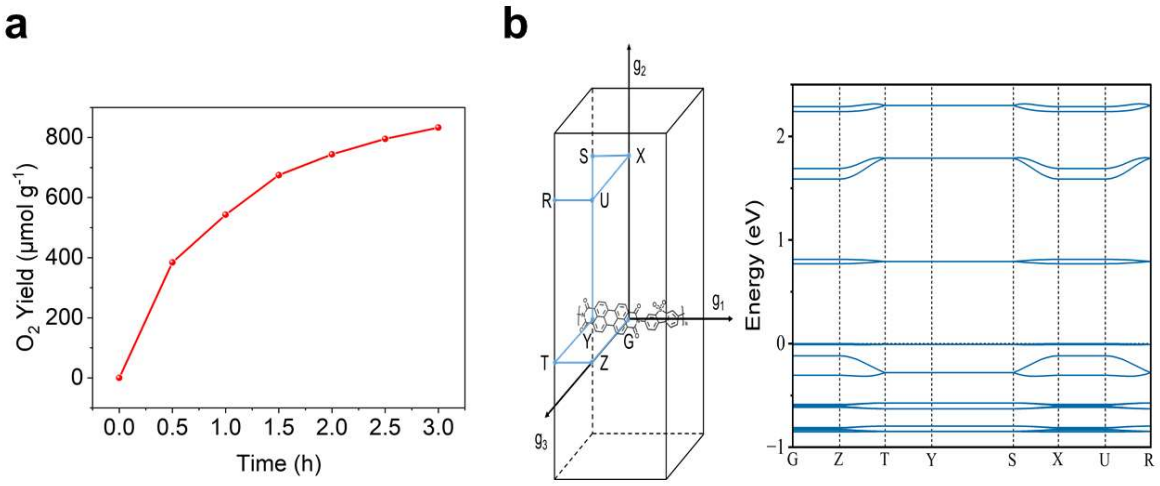

Figure S23. (a) Photocatalytic oxygen evolution performance and (b) corresponding first Brillouin zone (left) and Calculated electronic band structure (right) of PT-CS