

Electronic Supplementary Information for

A Heterostructure Photoelectrode Based on Two-Dimensional Covalent Organic Framework Film Decorated TiO₂ Nanotube Arrays for Enhanced Photoelectrochemical Hydrogen Generation

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S1. Synthesis and characterization of TiO₂ NTAs

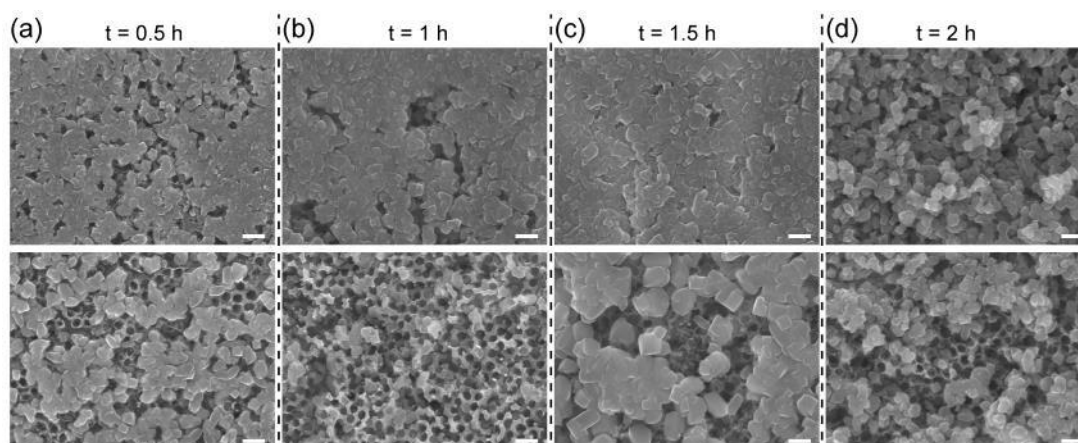


Figure S1. SEM images of TiO₂ nanostructures on Ti foil synthesized by anodization method. Anodization time: (a) 0.5 h, (b) 1 h, (c) 1.5 h, (d) 2 h. The scale bar size is 200 nm for all panels.

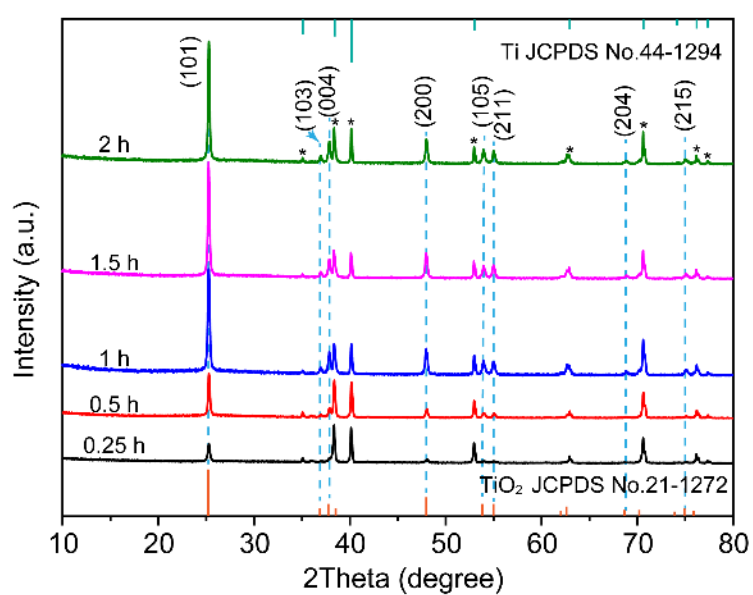


Figure S2. XRD patterns of TiO₂ nanostructures on Ti foil synthesized by anodization method at various reaction times. The * labels represented the typical diffraction peaks of substrate Ti foil.

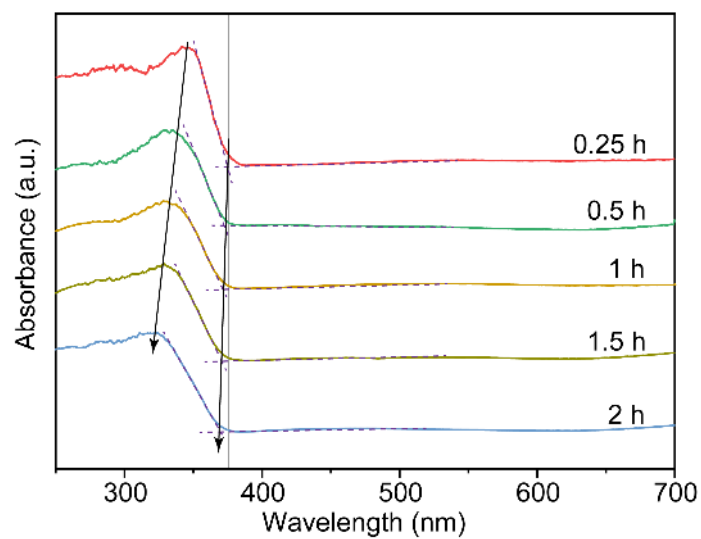


Figure S3. UV-vis diffusive reflection absorption spectra of TiO_2 nanostructures formed on Ti foil at various anodization times.

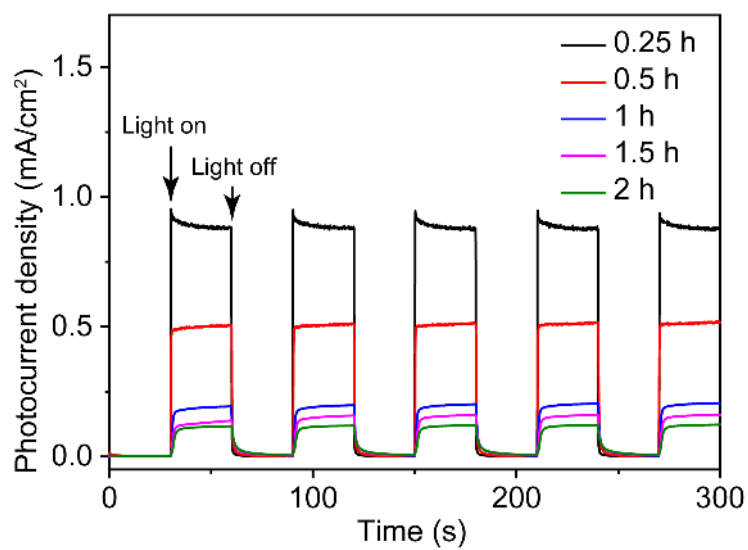


Figure S4. The transient photocurrent response of TiO_2 nanostructures formed on Ti foil at various anodization times. The photocurrent was recorded under full-range light irradiation.

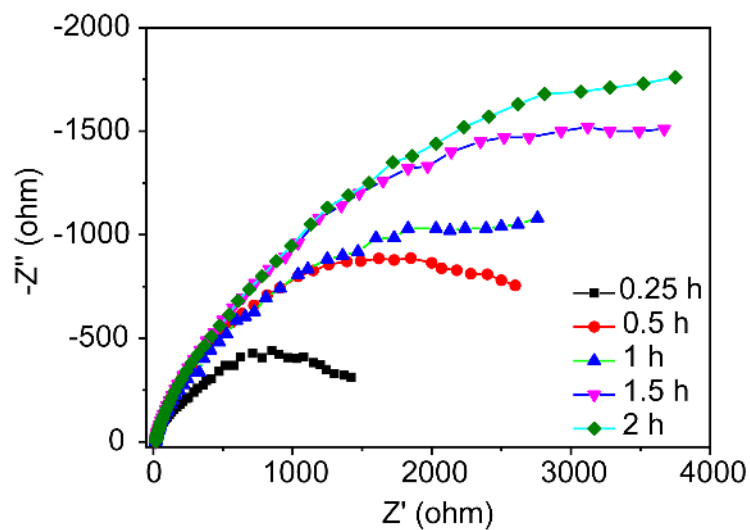


Figure S5. EIS Nyquist plots of TiO₂ nanostructures formed on Ti foil at various anodization times. EIS measurements were performed under full-range light irradiation.

S2. Fabrication of TpPa-1 COF films on TiO₂ NTAs

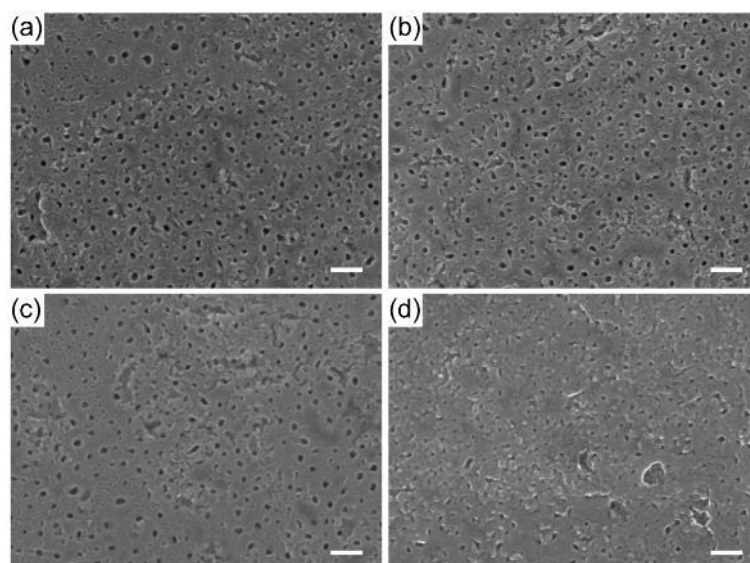


Figure S6. SEM images of TpPa-1/TiO₂-NTAs with (a) 0.4 mM Tp and 0.6 mM Pa, (b) 0.8 mM Tp and 1.2 mM Pa, (c) 1.5 mM Tp and 2.25 mM Pa, and (d) 2 mM Tp and 3 mM Pa. The scale bar size is 200 nm for all panels.

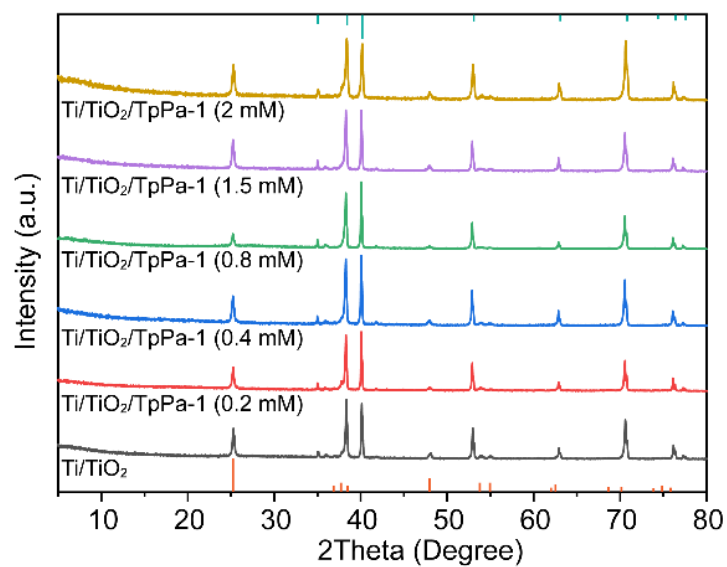


Figure S7. XRD patterns of TpPa-1/TiO₂-NTAs synthesized with different monomer concentrations (based on the concentration of Tp).

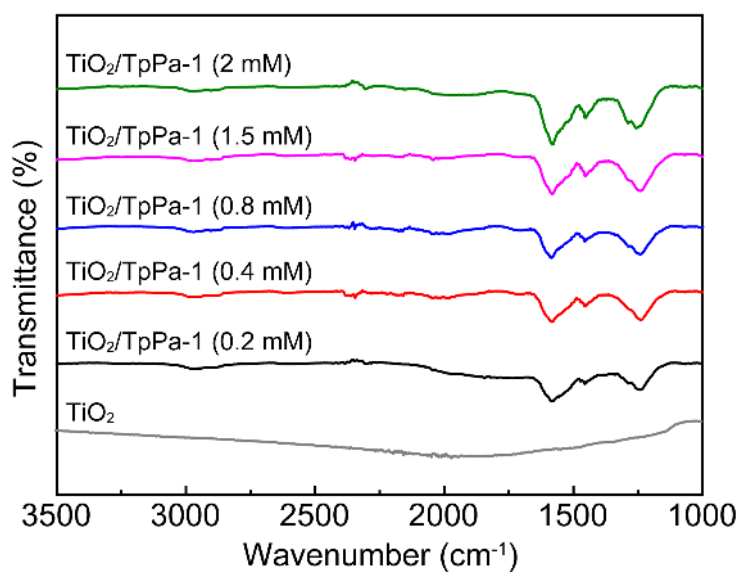


Figure S8. FTIR spectra of Ti/TpPa-1/TiO₂-NTAs synthesized with different monomer concentrations (based on the concentration of Tp) compared to TiO₂ NTAs.

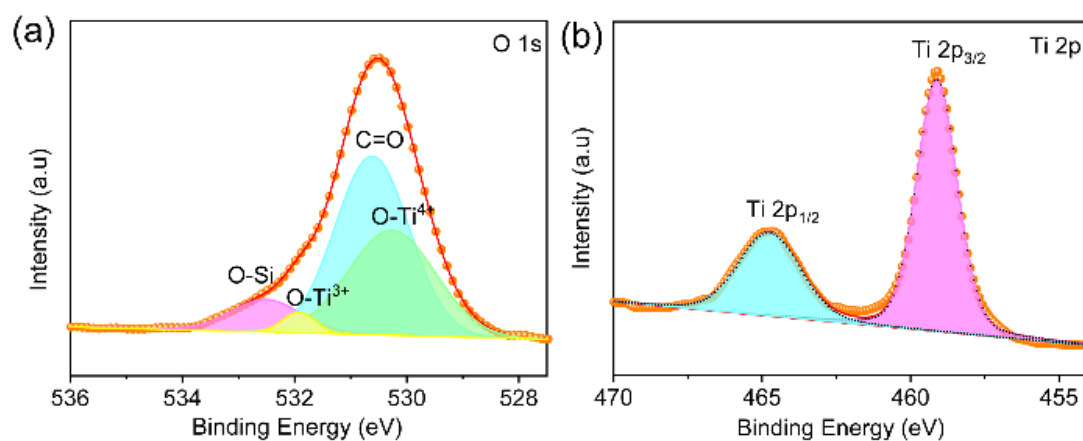


Figure S9. High-resolution XPS spectra of O1s and Ti2p cores of Pt₁@TpPa-1/TiO₂-NTAs.

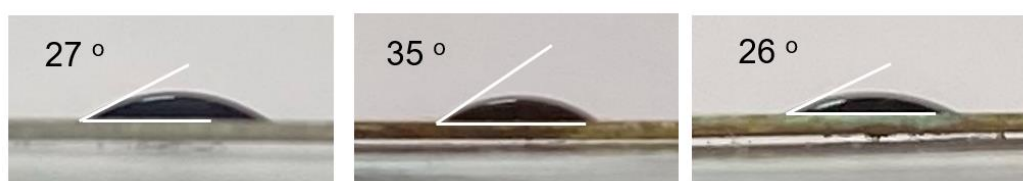


Figure S10. Contact angle measurements of TiO₂ NTAs (left), TpPa-1/TiO₂-NTAs (middle), and Pt₁@TpPa-1/TiO₂-NTAs (right).

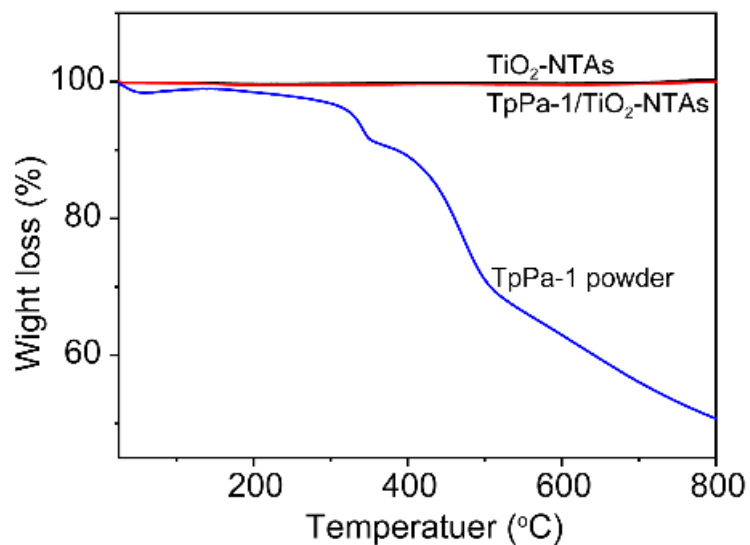


Figure S11. Thermogravimetric analysis (TGA) of TiO_2 NTAs and TpPa-1/ TiO_2 -NTAs compared to TpPa-1 powders. The TGA measurements were performed on a TechMax EXSTAR 700 Thermogravimetric Analyzer during the temperature range from room temperature to 800 °C with a ramp rate of 5 °C min⁻¹ under high-purity nitrogen conditions.

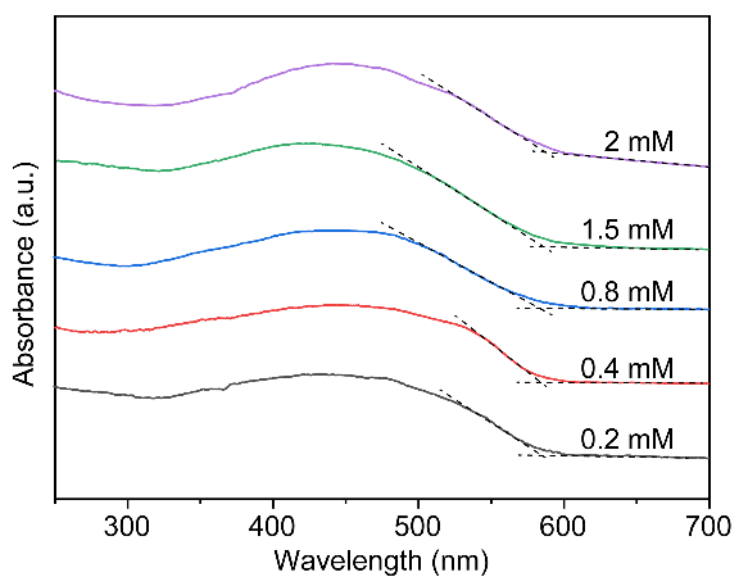


Figure S12. UV-vis diffusive reflection absorption spectra of TpPa-1/ TiO_2 -NTAs synthesized with different monomer concentrations (based on the concentration of Tp).

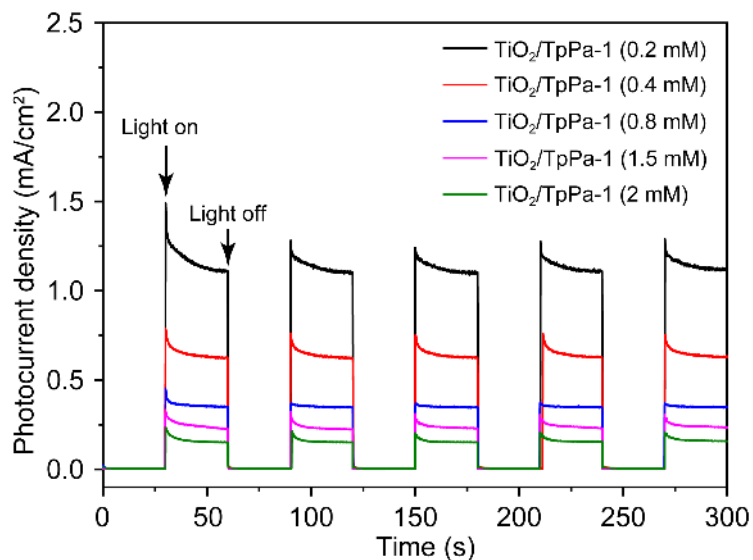


Figure S13. The transient photocurrent response of TpPa-1/TiO₂-NTAs synthesized with different monomer concentrations (based on the concentration of Tp). The photocurrent was recorded under full-range light irradiation.

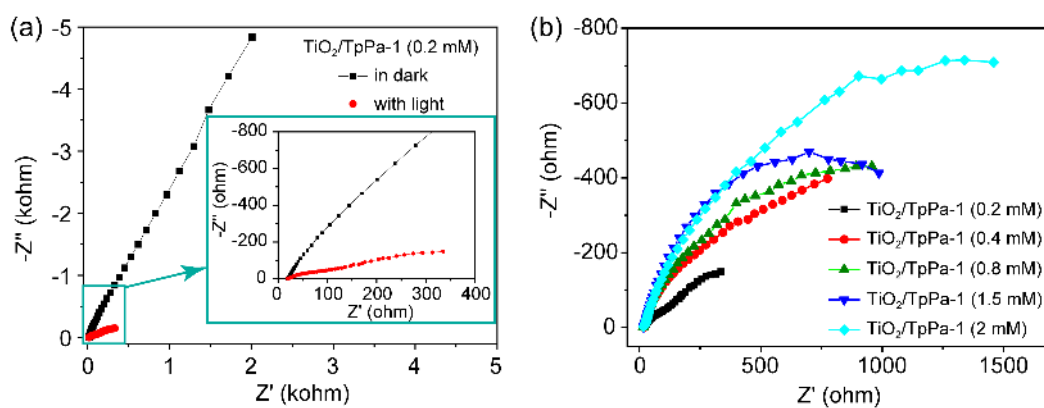


Figure S14. EIS Nyquist plots of (a) TpPa-1/TiO₂-NTAs (0.2 mM) electrodes in dark and with light irradiation, and (b) TpPa-1/TiO₂-NTAs synthesized with different monomer concentrations (based on the concentration of Tp).

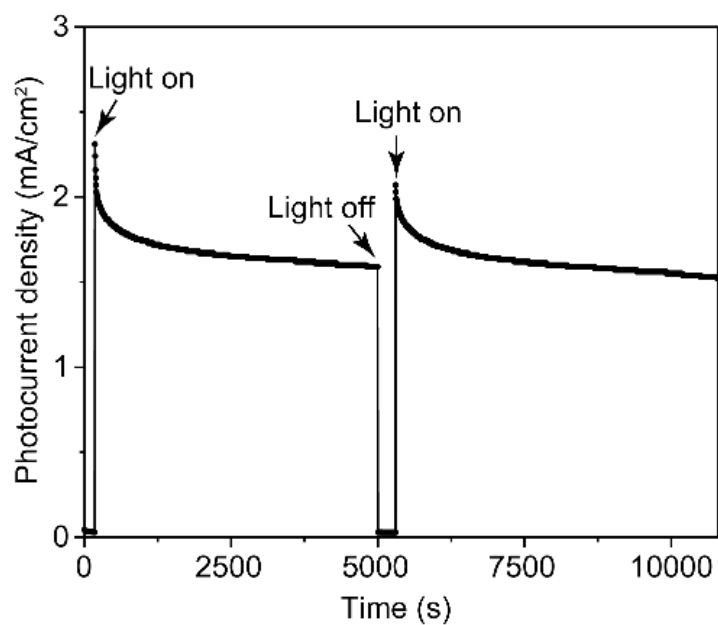


Figure S15. Time-dependent photocurrent density of $\text{Pt}_1@\text{TpPa-1}/\text{TiO}_2\text{-NTAs}$ photoelectrode under full-range light irradiation.

S3. Hydrogen evolution performance of $\text{Pt}_1@\text{TpPa-1}/\text{TiO}_2\text{-NTAs}$ electrodes.

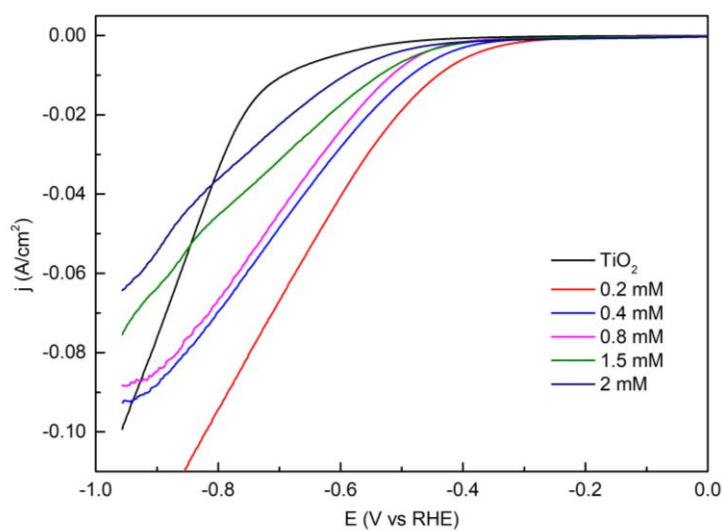


Figure S16. Linear scan voltammetry curves of $\text{TpPa-1}/\text{TiO}_2\text{-NTAs}$ electrode synthesized from different monomer conditions compared to TiO_2 NTAs under full-range light irradiation.

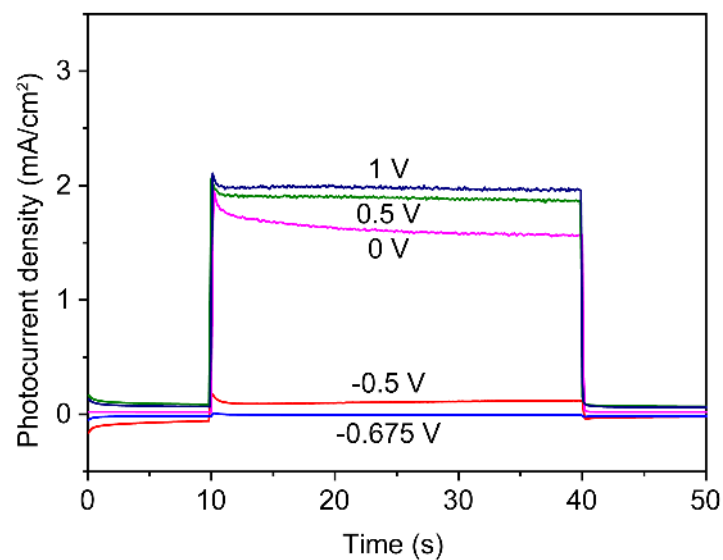


Figure S17. Transient photocurrent response of Pt₁@TpPa-1/TiO₂-NTAs photoelectrode under varying bias voltage vs. SCE.

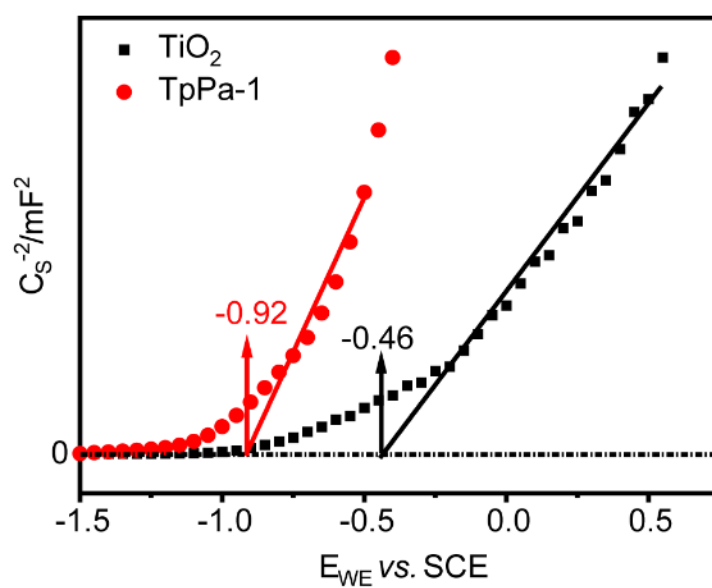


Figure S18. Mott-Schottky plots of TiO₂ and TpPa-1 measured in the dark at a frequency of 1 kHz in 0.5 M Na₂SO₄ aqueous solution.