

Light-assisted electrochemical water-splitting at very low bias voltage using metal-free polythiophene as photocathode at high pH in a full-cell setup

Kouki Oka¹, Orië Tsujimura¹, Takeo Suga¹, Hiroyuki Nishide¹, Bjorn Winther-Jensen²

¹Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan.

²Department of Advanced Science and Engineering, Waseda University, Tokyo 169-8555, Japan

Supporting Information

Resistance measurements of neutral IVP-PTTh films

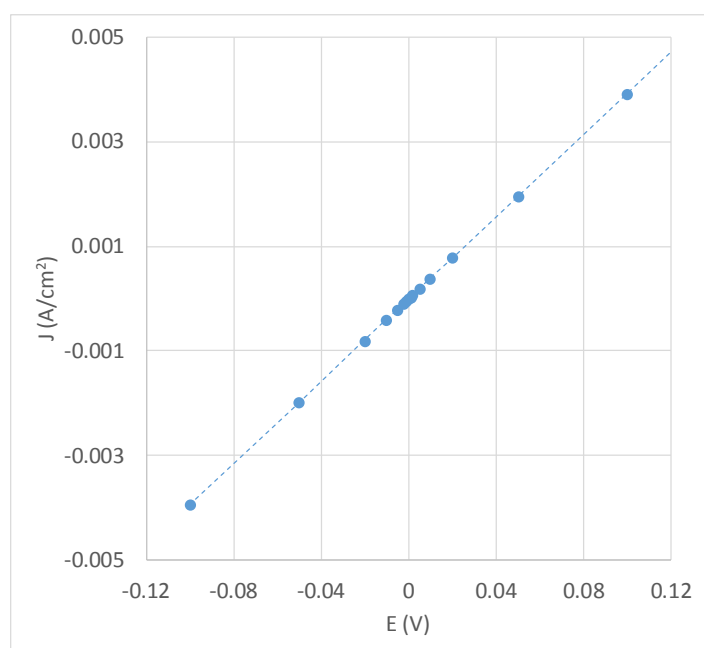


Figure S1. I-V curve of IVP-PTTh on glassy carbon measured by Chronoamperometry (CA) at different applied voltage. The resistance was calculated using Ohm's law as E/J . Please note that the measurement in figure S1 is including the resistance of the glassy carbon substrate.

PTTh nanowalls

The **PTTh** film with nano-walls was polymerised using a 15 w/v% Fe(III) p-toluenesulfonate in butanol as the oxidant solution. Approximately 0.5 mL of this solution was spin-coated onto a glassy carbon substrate (polished to a mirror finish) at 1500 rpm for 30 s. The deposited sample was then placed in a pre-heated VPP chamber with **BTh** and **TTh** (**BTh**:**TTh** = 1:5 w/w) monomer and left to polymerise in the oven at a temperature of 120 °C for 2 h. The sample was then taken out and washed and left to soak overnight in ethanol. After soaking the sample was rinsed once more and left to dry in air.

During the polymerisation process a **PBTh** layer is firstly formed upon which the **PTTh** nanowalls are formed. For further information regarding the polymerisation process please see reference 1.

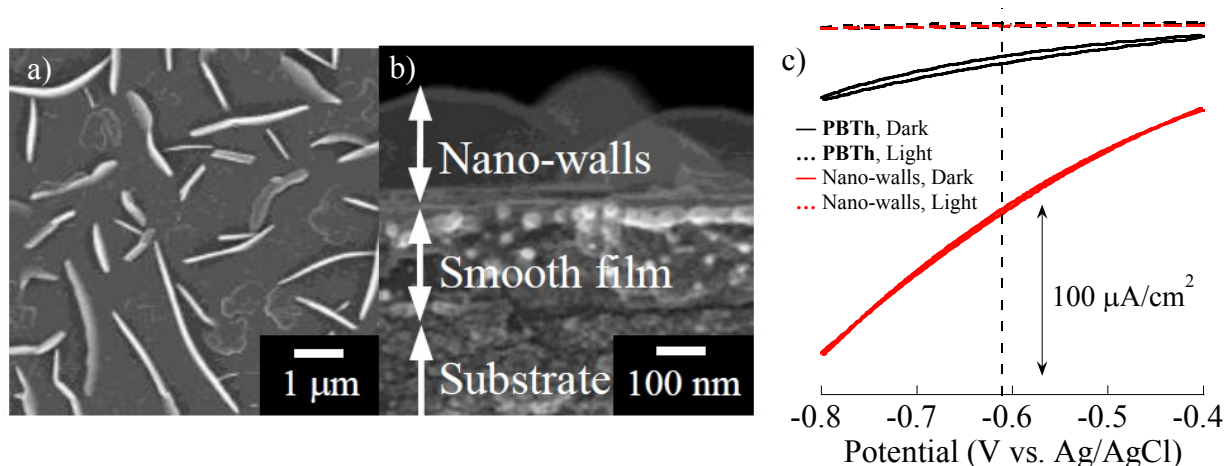


Figure S2 PTTh nanowalls a) SEM of surface, b) cross-section (PTTh nanowalls atop smooth PBTh layer) and c) CV of PTTh nanowalls with without and with light, compared to the smooth PBTh film alone. 20 mV/s in 0.1M phosphate buffer pH 6.8. The dotted vertical line indicated the equilibrium reduction potential for water-reduction at pH 6.8.

Iodine Vapour-assisted Polymerisation (IVP) of TTh

PTTh films were polymerised after spin-coating of TTh (from TCI) from solution. Approximately 0.5 mL of solution was spin-coated onto a glassy carbon substrate (cleaned by UV-Ozone) at 1500 rpm for 25 s. The TTh coated sample was then placed in a pre-heated VPP chamber with iodine (from TCI) and left to heat and polymerise in the oven at a temperature of 90 °C for 1 h. The sample was then taken out and washed and left to soak overnight in acetonitrile. After soaking the sample was rinsed once more and left to dry in air.

Substrates

Each substrate was sonicated in Chloroform for 1 h, rinsed in acetone, and cleaned by UV-ozone prior to polymerisation. Polymerisation was conducted as per before save glassy carbon was replaced with the appropriate substrate.

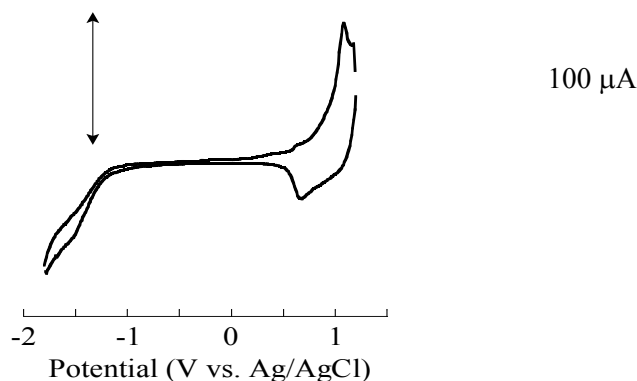


Figure S3. CV of IVP-PTTh in AN, 0.1M TBA-PF6. Scanrate 50mV/s.

XPS measurements

X-ray photoelectron spectroscopy (XPS, JPS-9010TR) with Mg K and Al K radiation was carried out on IVP-PTTh coated onto glassy carbon. The electron binding energy of the XPS was referred to the C 1s peak at 284.6 eV. XPS intensities were calculated by integrating peak areas after background subtraction.

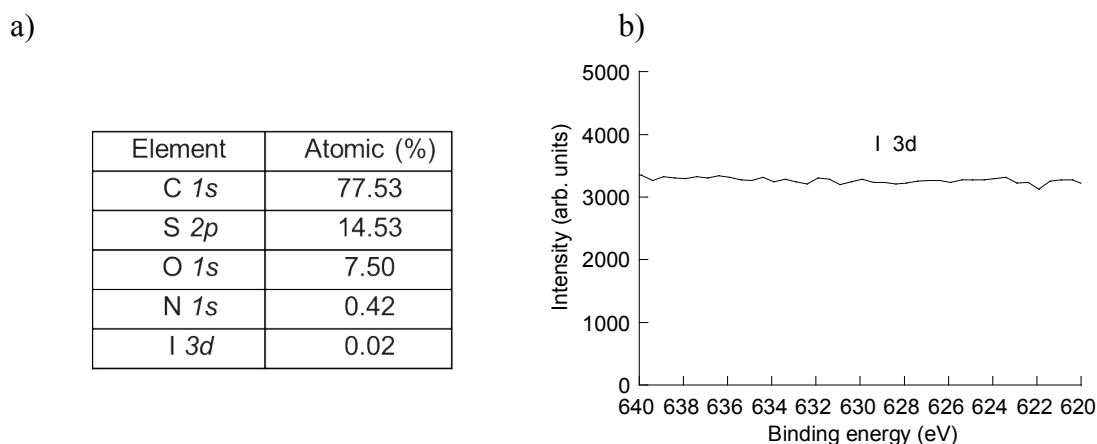


Figure S4. a) Table of atomic % of the elements found in the IVP-PTTh film, b) Zoom-in of the iodine (3d) binding energy range.

Selection of solvent

When testing the IVP-PTTh films as photo-electrocatalysts for the HER it was soon realized that the solvent and solution strength of the TTh spin-coating solution had a strong influence on the morphology of the PTTh films and thereby on their photo-electrocatalytic performance. The spin-coating and polymerization conditions were therefore optimized [see figure S5, S6 and S7], which resulted in an optimal coating thickness of 75nm with chlorobenzene as the preferred solvent.

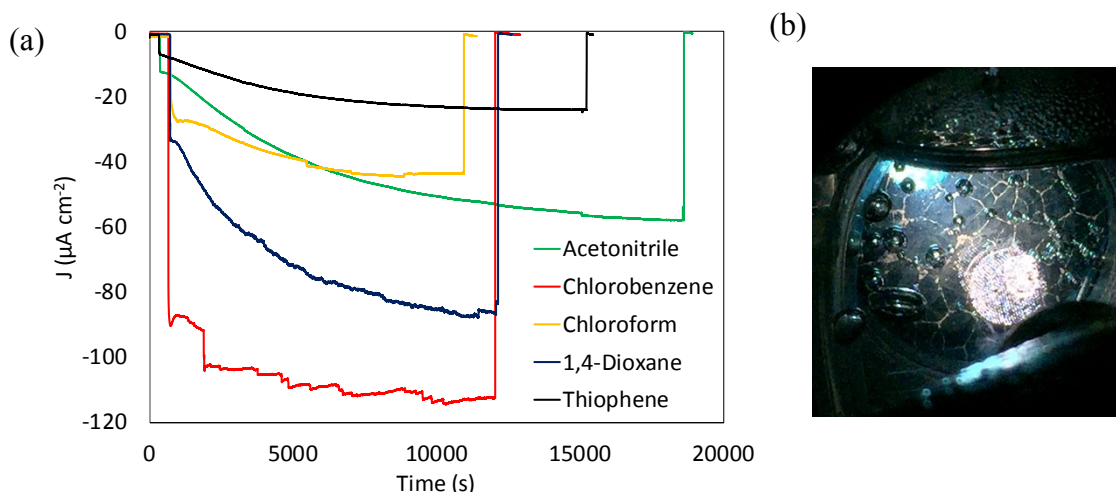


Figure S5. Optimization of IVP-PTTh films by changing the solvent for the TTh spin-coating solution (a) Chronoamperograms at -0.5V vs Ag/AgCl of IVP-PTTh in 0.1M phosphate buffer pH 6.8 and (b) photograph of the formation of H₂ bubbles on a sample made using chlorobenzene as solvent for the spin-coating solution.

The morphology is influencing two properties, which – unfortunately – has opposite effect on the performance: Smooth thin films have low resistance (short distance to the substrate) but low interface area to water (fewer reaction sites per geometric area). For rough films it is obviously the other way around. The different solvents investigated resulted in different morphology of the IVP-PTTh, (Figure S6) which helps explain the significant differences in electrocatalytic performance depending on solvent described above.

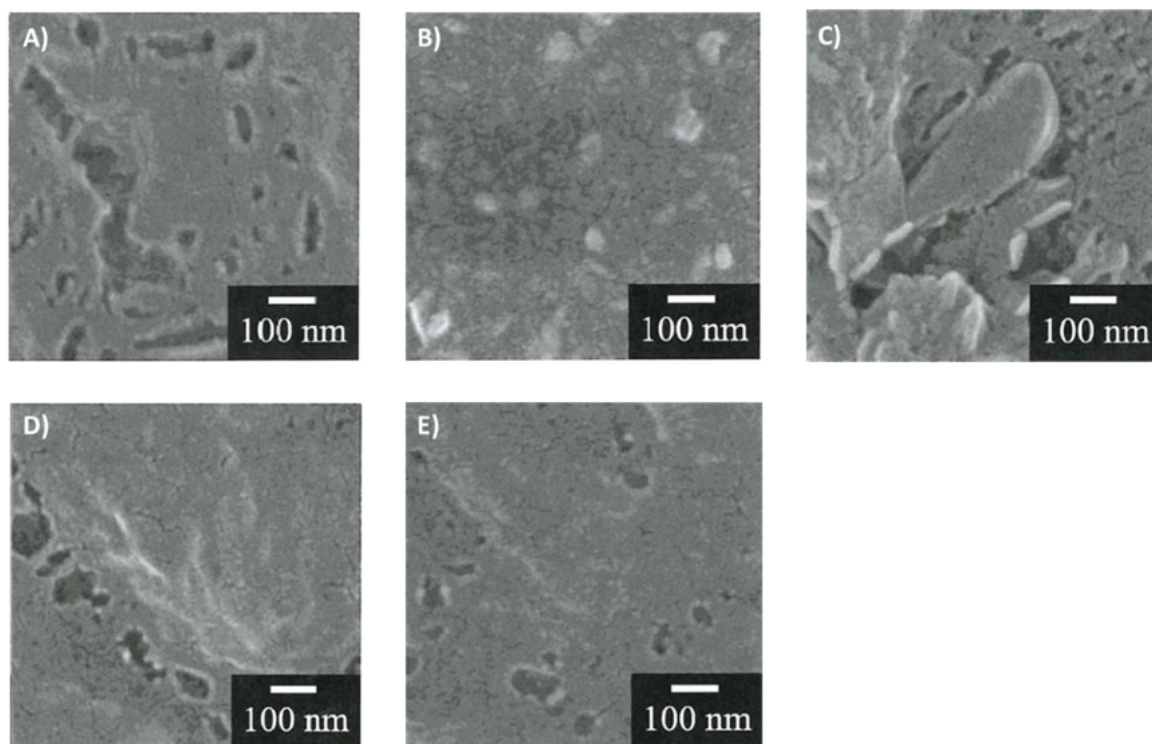


Figure S6. SEM images of IVP-PTTh films using various solvents for the TTh spin-coating solution. A) Acetonitrile, B) Chlorobenzene, C) Chloroform, D) 1-4-Dioxane, E) Thiophene.

Optimizing film thickness

For the preparation of the thin PTTh films the solution (50 mg/mL terthiophene in chlorobenzene) was diluted with chlorobenzene to a concentration of 40 mg/mL, 30 mg/mL, 20 mg/mL, and 10 mg/mL terthiophene for the 75 nm, 55 nm, 30 nm, and 15 μm film respectively. Polymerisation then occurred via the standard technique described above.

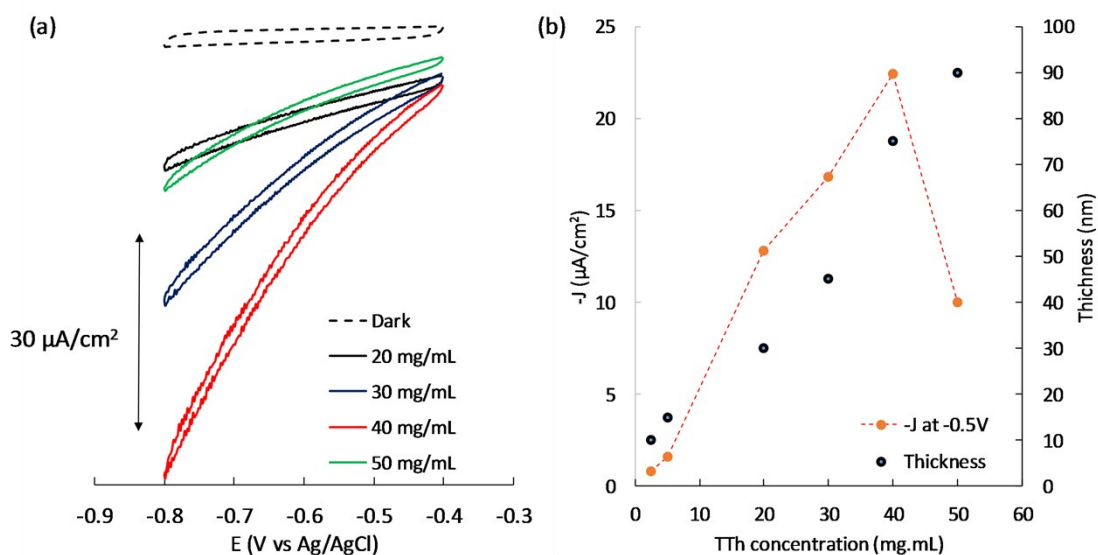


Figure S7. Optimization of IVP-PTTh films with regard to thickness by changing the concentration of TTh in chlorobenzene for the spin-coating solution. (a) Cyclic voltammograms of PTTh samples at 20mV/s on 0.1M phosphate buffer pH 6.8 and (b) Thicknesses of the obtained films with different monomer concentration (from S4(a)) compared to the current density at -0.5V vs Ag/AgCl.

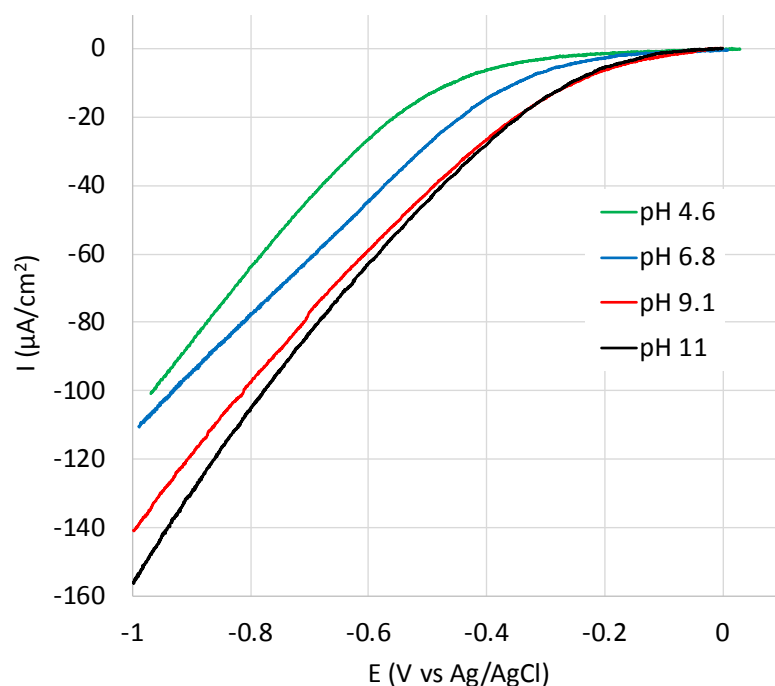


Figure S8. Cyclic voltammetry at 1 mV/s under light at different pH (forward sweeps). Electrolyte solution strength was in all cases 0.1M phosphate ions.

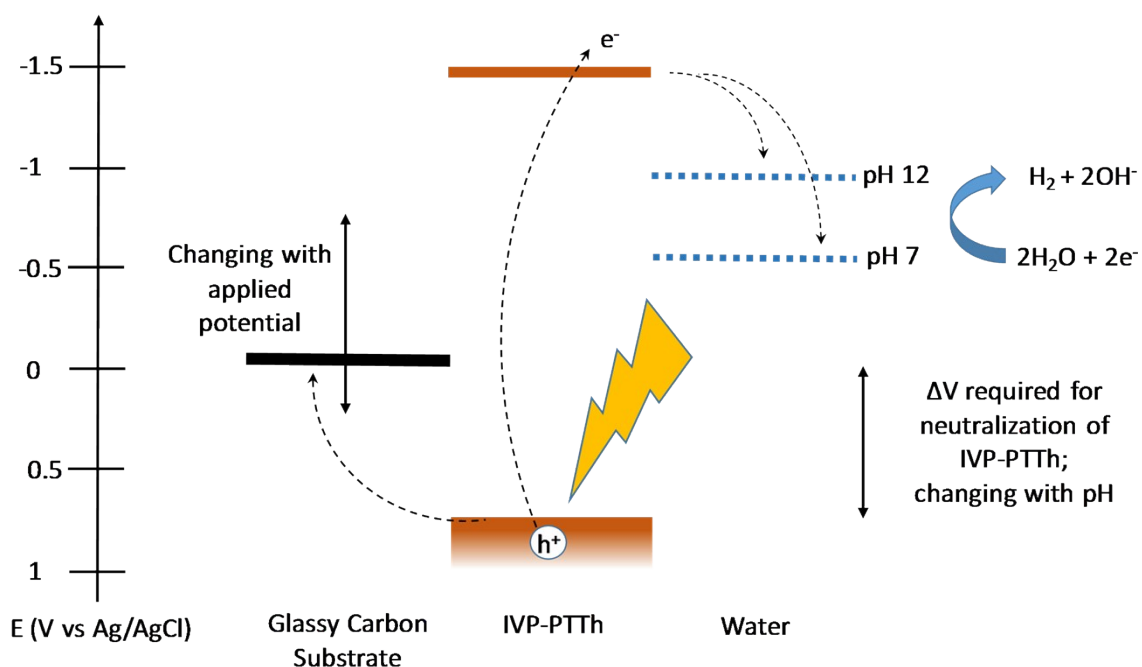


Figure S9. Energy diagram (versus Ag/AgCl) and proposed charge transfer for the light-enhanced hydrogen evolution on IVP-PTTh. The influence of pH and applied potential on the energy levels are sought included in the diagram. It can be seen, that even at high pH there is a significant potential difference between the LUMO level and E_o for the water reduction reaction.

Preparation of MnO_x Films

MnO_x Films were prepared according to literature procedures.^{[2][3]} Ethylammonium nitrate (EAN) was firstly prepared by neutralising ethylamine with dilute nitric acid, followed by removal of the water under reduced pressure using rotary evaporation at 70°C for 2 hours. The manganese oxide (MnO_x) films were prepared by electrodeposition in a three-electrode electrochemical setup from EAN. The deposition electrolyte (50 ml in volume) contained 10 mM Mn(CH₃COO)₂ in a 1:9 water to EAN mixture. It was acidified slightly by adding 125 µl of 4.0 M HNO₃ to give 10 mM excess acid. Fluorine-doped tin oxide (FTO) conducting glass with an area of 5 cm x 3 cm was used as substrate for film deposition (area of deposition was 2.5 cm x 3.0 cm). The MnO_x film was electrodeposited at 120 °C by applying a constant current density of 200 µA/cm². A time of 5 min was used to prepare the films. After deposition, the films were rinsed thoroughly with distilled water.

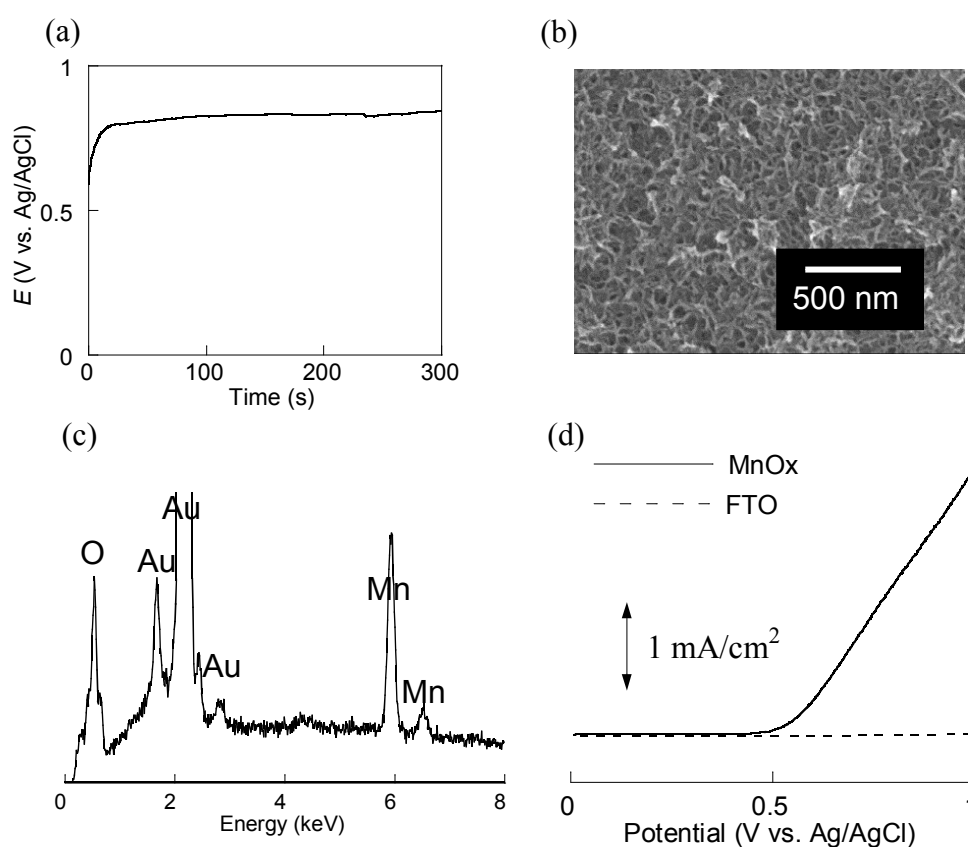


Figure S10. (a) Chronopotentiogram of 10 mM Mn(CH₃COO)₂ in EAN/water containing 10 mM HNO₃. (b) SEM surface image of MnO_x film on FTO substrate. (c) Typical EDX spectrum of MnO_x film on Au substrate, acquired at 25 kV a working distance of 15 mm. (d) Linear Sweep voltammograms of MnO_x film on FTO substrate in 1 M NaOH in water at the scan rate = 10 mV/s.

Full-cell testing

The full-cell testing was performed in a custom build two-compartment “tandem” setup made from PVC [Figure S11a]. PTTh films on glassy carbon were used as cathode and MnOx on FTO as anode in a two-electrode configuration. The PTTh was connected as working electrode and MnOx as both counter and reference electrode. An initial CV was performed to check photo-electro-catalysis before CA measurements at different bias potentials. Light was only shone on the PTTh cathode. 5 mL gas chromatography (GC) injections into the gas chromatograph (GC-8A, Shimadzu, MS-5A column, Ar carrier) was performed and the resulting hydrogen peak recorded. The rate of hydrogen production was calculated (Ar flow rate 5 mL min^{-1}) for conversion to faradaic efficiency.

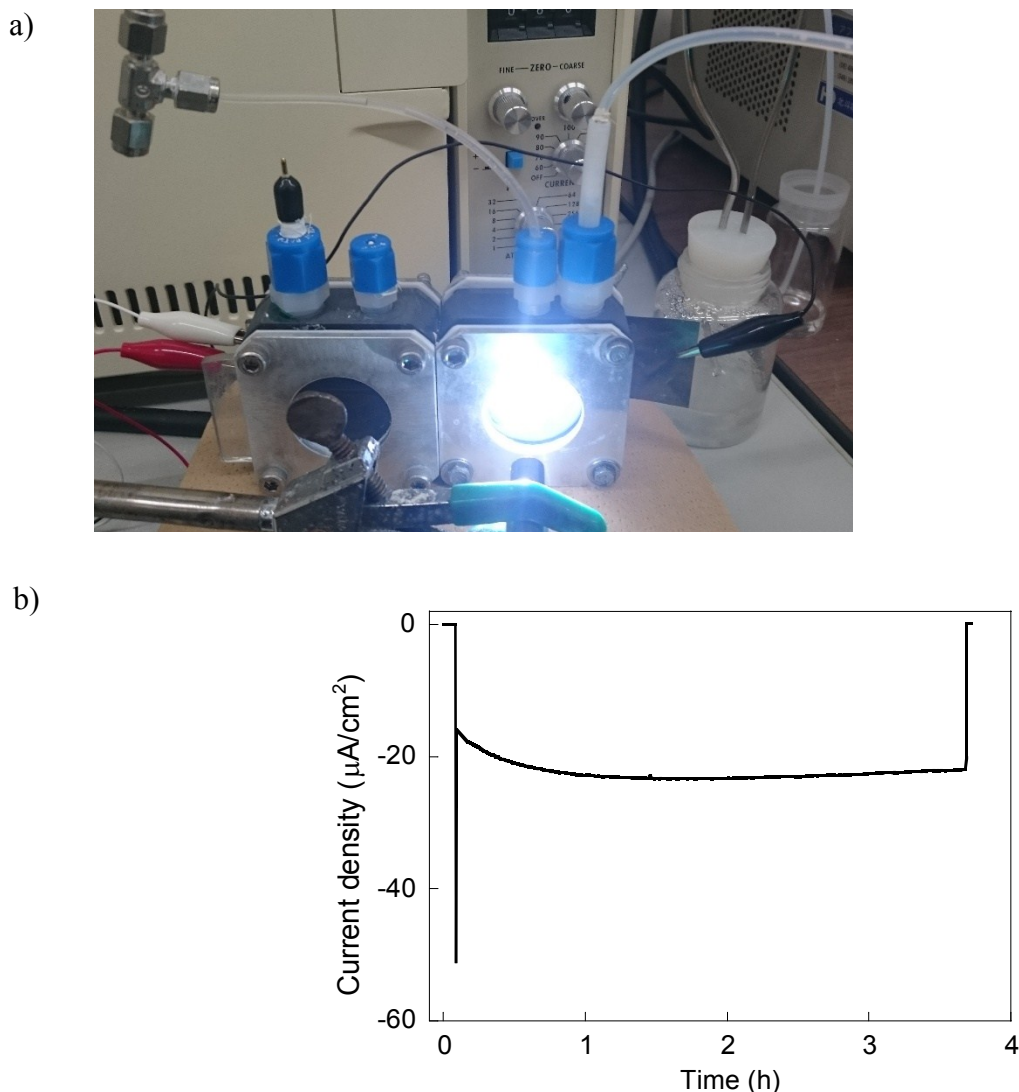


Figure S11. a) Photograph of the two-compartment “tandem” cell used for two-electrode electrochemical testing of IVP-PTTh under light at high pH with MnOx as combined counter and reference electrode. b) Measurements with tandem cell at pH 12 (0.1M Sodium phosphate/Sodium hydrogen-phosphate buffer) using IVP-PTTh (under light) and MnOx as cathode and anode respectively. CA measurements under light with applied bias-potential of 1.23 V (vs MnOx).

MALDI

Matrix Assisted Laser Desorption/Ionization (MALDI, AUTOFLEX (Bruker)) was performed on IVP-PTTh coated onto ITO substrate.

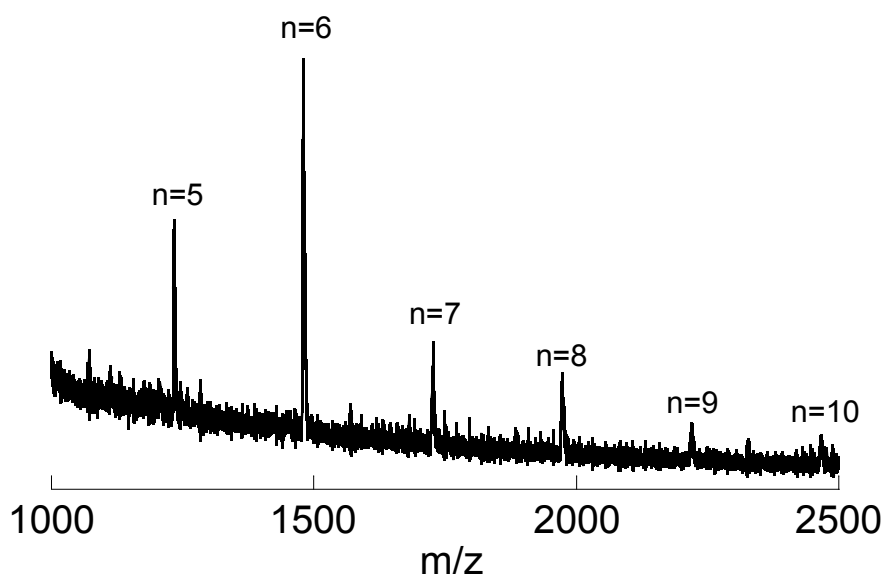


Figure S12. MALDI spectra of IVP-PTTh. “n” refers to number of TTh units in a segment thus the difference between the main segment peaks is 246 g/mol.

Raman spectroscopy

Measurements with 532nm and 785nm laser was performed. The latter to better observe possible FeOx impurities found in the 200-700 cm^{-1} range^[4].

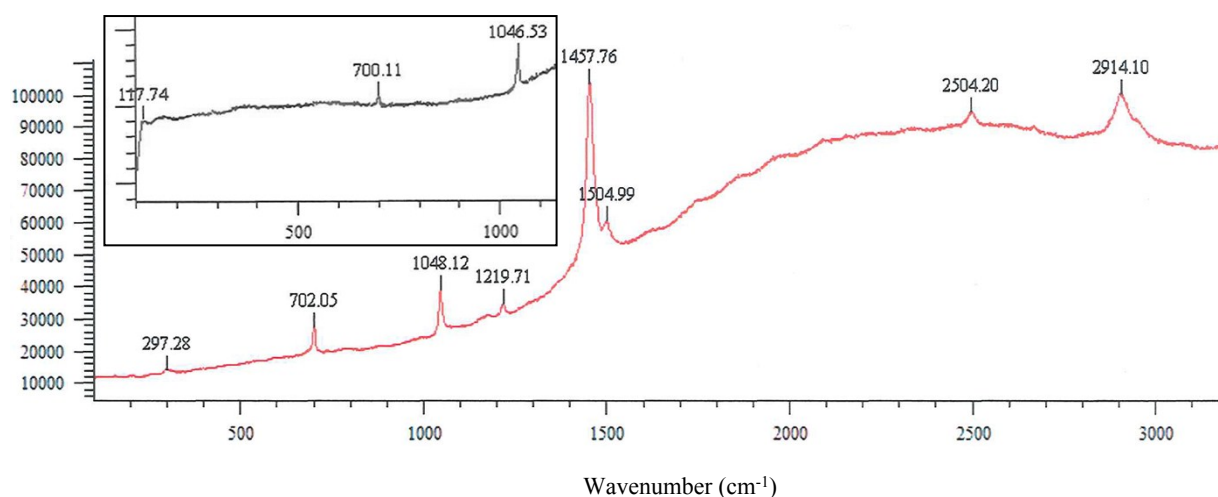


Figure S13. Raman spectra of IVP-PTTh thin-film. Raman laser wavelength 532nm. Typical polythiophene peaks: C=C ring stretching (1505 and 1458 cm^{-1}), C-C inter-ring stretching (1220 cm^{-1}), C-H stretching (1048 cm^{-1} and 2914 cm^{-1}) and C-S-C ring bending (702 cm^{-1}). No baseline correction. Background intensity due to fluorescence from the IVP-PTTh (532nm is within the absorption range of the polymer). Insert: measurement with 785nm laser.

Electrochemical testing

Except for the full-cell experiments, a standard three-electrode setup was used. Unless otherwise stated, the counter and reference electrodes used was glassy carbon and Ag/AgCl respectively. An initial CV scan was performed for all samples prior to testing to confirm photo-electro-catalytic behaviour. Illumination was provided by an Asahi Spectra Co. MAX-302 300W Xe lamp with an equivalent power of 1.0 sun.

Electrolytes and pH

Phosphate solutions with different pH were made up using varying ratios of NaH_2PO_4 and Na_2HPO_4 and dissolved in water. At pH 9, the solution was almost entirely Na_2HPO_4 . 10 mol L^{-1} NaOH was added to increase alkalinity for pH 11, 12, and 13. The pH of each electrolyte solution was tested prior to the studies using a Mettler Toledo pH meter. Testing at various pH was conducted on the same PTTh film but a new area was utilised for each electrolyte. Ar was bubbled through the cell for 20 min prior to testing, followed by the main CV and CA test.

Interaction between light and PTTh

CV and CA measurements on the glassy carbon PTTh films were run under Ar (5 mL min^{-1}) to assess the performance of the film. CA measurements were conducted by applying a potential of $-0.5 \text{ V vs. Ag/AgCl}$ over a period of 3 hours under illumination. GC measurements were conducted concurrent to CA. UV-Vis spectroscopy of the PTTh films polymerised on glass slides were conducted on a Jasco V670 Spectrophotometer to determine the absorbance.

Material characterisation

Scanning electron microscopy (SEM) images (accelerating voltage of 5 kV) and energy dispersive X-ray spectroscopy (EDS, accelerating voltage of 25 kV) were taken using the HITACHI S-4500S SEM and the HITACHI S-3000N SEM. XRD spectra were recorded using Rigaku RINT-Ultima.

A Renishaw inVia Reflex Raman system with a 532 nm green and 785 nm diode laser was used for Raman characterisation.

The thickness of the polymer film was measured using a KLA Tencor.

The resistance of the as-polymerized PTTh films were conducted using a two-line setup. A glass-slide with two gold lines coated in 2.5 cm distance allowed for direct resistance measurement (using a multimeter) of PTTh films on 2.5 cm wide glass-slides, giving a sheet resistance in Ohm/sqr .

The resistance through PTTh film on glassy carbon was measured in a DC setup after removal of Iodine from the PTTh by washing in acetonitrile (before any electrochemical measurements). Gold-coated mylar was sandwiched with the PTTh coated glassy carbon between two glass slides. Care was taken to prevent any contact between edges of the glassy carbon and the gold. The I-V measurement showed a linear correlation, confirming ohmic conditions (Figure S1). The measurement was done in triplet for both coated and uncoated glassy carbon and the average resistance was $4.2 \text{ Ohm}\cdot\text{cm}^2$ for 75 nm thick PTTh films (after subtracting the average value for the uncoated glassy carbon substrates).

References

- 1) Kolodziejczyk, B., Winther-Jensen, O., Ng, C. H., Lin, S., Bao, Q., and Winther-Jensen, B. (2014) Growth of polythiophene nano-walls and their unique electrochemical and optical properties, *Materials Horizons* 1, 452-460.
- 2) F. Zhou, A. Izgorodin, R. K. Hocking, L. Spiccia, D. R. MacFarlane, *Adv. Ener. Mater.*, **2012**, 2, 1031-1021.
- 3) F. Zhou, C. M.-Worth, H. Li, J. Li, L. Spiccia, D. R. MacFarlane, *J. Mater. Chem. A*, **2015**, 3, 16642-16652.
- 4) Panta and Bergmann, *J Material Sci Eng* **2015**, 5, 1.