- SUPPLEMENTARY MATERIAL -

A Light-Assisted, Polymeric Water Oxidation Catalyst that Selectively Oxidizes Seawater with a Low Onset Potential

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Preparation of PEDOT-1 by vapour phase polymerisation

PEDOT doped with a sulphonated Mn tetraphenyl porphyrin (PEDOT-**1**) were successfully deposited onto ITO-coated PET sheet via a modified Chemical Vapour Phase Polymerisation (VPP) approach. In a typical VPP process, a thin oxidant film was coated onto ITO-coated PET sheet substrate by spin-coating a dichloromethane solution containing Iron(III) p-TS and sulphonated Mn tetraphenyl porphyrin (**1**) with a mole ratio of 3:1. Then the modified ITO-PET sheet was transferred into the vapour phase polymerisation chamber with EDOT monomer vapour set-up in oven at 60 °C for VPP of PEDOT for 30 mins. After VPP, the as-prepared PEDOT-**1** film on ITO-PET was washed with both ethanol and Milli-Q water in order to achieve quality thin films. The as-synthesised PEDOT-**1** thin film shows a green colour, which is usually blue compared with typical pure thin PEDOT films. This could be attributed to the incorporation of Mn-porphyrin in the PEDOT matrix. For control experiments, the pure PEDOT films were also prepared under identical conditions without sulphonated Mn tetraphenyl porphyrin (**1**).

Characterization of PEDOT-1:

1. Flexibility – Digital images of PEDOT-1 coated ITO-PET.

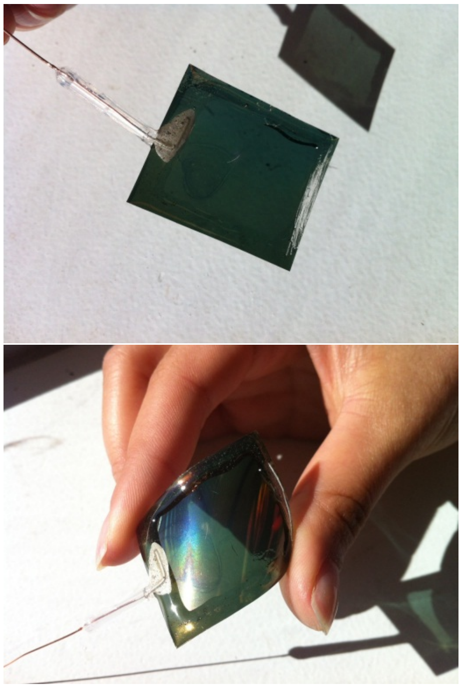

Fig. S1. Digital images of the as-prepared flexible electrode comprising PEDOT-**1** thin film deposited onto ITO-coated PET.

2. Morphology – SEM image of PEDOT-1 film

The morphology of PEDOT-**1** film was characterised by using a field emission SEM with EDS (FESEM, JEOL 7500). Fig. S2(a) shows the typical SEM image of PEDOT-**1** film deposited on the ITO-PET electrode, showing a highly porous surface structure with a thickness around 500 nm. In addition, the EDX-mapping image shown in Fig.S2(b) indicates uniform distribution of sulphonated Mn-porphyrin (identified as Mn element) in the PEDOT polymer matrix, which is important for further catalytic performance.

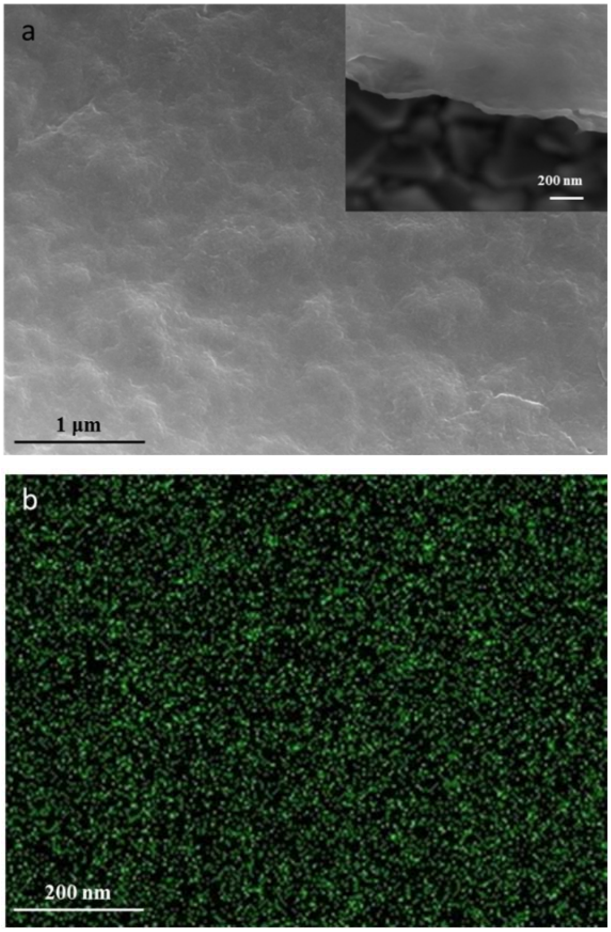

Fig. S2. (a) High-Resolution Scanning Electron Micrograph (HRSEM) of PEDOT-**1** thin film, and (b) EDX-ray mapping image of Mn in PEDOT-**1** in the same area.

3. UV-Visible measurements on PEDOT-1 and 1

UV-Visible spectroscopy (UV-1800 Spectrophotometer, SHIMADZU) was further used to confirm the presence of sulphonated Mn porphyrin **(1)** in the PEDOT matrix of PEDOT-**1**. It clearly shows the enhanced light absorption of in the range of 350 to 500 nm, which could be assigned to sulphonated Mn porphyrin (**1**).

4. Photocatalytic studies on PEDOT-1

A standard photo-electrochemical cell was used to study oxygen evolution. The gas inlet and outlet were used for N_2 gas flow to de-oxygenate the solution before the test and provide a constant external pressure of N_2 during the experiments. Electrochemical measurements were performed using an eDAQ electrochemical hardware system consisting of e-cordor 401 and eDAQ Potentiostat with eDAQ Chart/ eDAQ EChem software (AD Instruments).

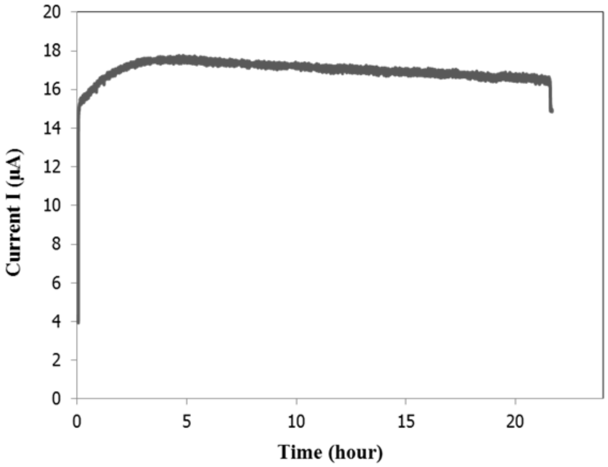

Fig. S3. Current over 24 h under illumination, by PEDOT-**1**/ITO-PET in seawater, at an applied potential of +0.70 V (vs. Ag/AgCl; Pt counter electrode).

5. Overnight testing of PEDOT-1

In order to ensure that the generated oxygen derived from catalytic water oxidation and not from another process involving degradation of the electrode materials, PEDOT-**1**/ITO-PET was subjected to 24 h testing under illumination in seawater. The resulting data is shown in Fig. S3. As can be seen, a steady current was obtained. This is consistent with a catalytic effect and indicates that no chemical degradation occurs even after 24 hours of oxygen evolution. This result is not unexpected. Porphyrin or polymer degradation normally involves over-oxidation, which would consume, not release O_2.

6. Independent testing for Cl_2 in solutions.

To independently inspect for the presence of chlorine, a commercial analytical test strip (Merckoquant®)

was used, which is capable of detecting 0.5mg Cl_2/L solution. The typical test was made by immersing one piece of test stript into the solution to monitor the colour change of the stript. In all testing cases, no colour change was observed.

7. Electrochemical Impedance Spectra (EIS) of PEDOT-1.

The electrochemical impedance spectra (EIS) measured with and without light illumination applied to the photo-electrochemical cell using a Solartron SI1260 Impedance Analyzer. The ac amplitude was 5 mV. The frequency range applied was 100 KHz – 0.01 Hz.The features of the impedance spectra are indicative of time constant and the characteristics varied with light on and off.

The equivalent circuit presented as below (Fig. S4) was used to fit the EIS data obtained (1) at +0.7V with and without light stimulation, and (2) at different potentials, +0.70V, +0.75V, and +0.80V, respectively (as shown in Fig. 7). Because the capacitance and resistance of PEDOT are not negligible, we used an equivalent circuit composed of 2RC elements in series which account for the PEDOT-**1** layer (CPE1, R1) and the charge transfer process (CPE2, Rct) to interpret the EIS. The fitted data are shown in Table S1. It is clear that the presence of light facilitates the charge transfer process at the electrode which was confirmed by the decrease of charge transfer resistance, Rct, under illumination compared with that measured in dark. We found with the increase of the applied potential, the charge transfer resistance (Rct) significantly decreased under light illumination.

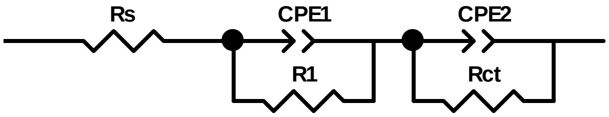

Fig. S4. The equivalent circuit used to fit the EIS data presented in Fig. 7. Rs- uncompensated resistance. CPE1, R1- capacitive (constant phase element) and resistive parameters of photoelectrochemical electrode. CPE2, Rct- double layer capacitive (constant phase element) parameter and charge transfer resistance.

Table S1.

	Rs/Ω	CPE1		R1/Ω	CPE2		Rct/Ω
		CPE-T/F	CPT-P		CPE-T/F	CPE-P	
0.7 V (dark)	10.05	3.41×10^{-5}	0.90	26.54	1.07×10^{-3}	0.94	8.26×10^{4}
0.7 V (light)	9.83	3.10×10^{-5}	0.79	28.79	3.51×10^{-3}	0.86	1.67×10^{3}
0.75 V (light)	9.35	6.41×10^{-5}	0.74	23.02	3.69×10^{-3}	0.83	6.40×10^{2}
0.85 V (light)	9.23	1.25×10^{-4}	0.70	19.06	4.49×10^{-3}	0.75	2.49×10^{2}

8. Converting potentials vs Ag/AgCl to the NHE and RHE scales.

Potentials vs. the Ag/AgCl reference electrode were converted to the normal hydrogen electrode (NHE) scale using the equation:[1,2]

$$V_{NHE} = V_{Ag/AgCl} + 0.22\ V$$

Potentials vs. the Ag/AgCl reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation:[1,2]

$$V_{RHE} = V_{Ag/AgCl} + 0.22\ V + 0.059 \times pH$$

Thus, at pH 7:

$$V_{RHE} = V_{Ag/AgCl} + 0.22\ V + 0.413\ V$$

Synthesis, processing, and spray-deposition of chemically-polymerised, solution-processed PEDOT-1 (containing PSS for effective dispersion)

PEDOT:PSS was synthesised by a literature procedure[3] involving chemical oxidation of ethylene dioxythiophene (EDOT) with ammonium persulfate (APS) in the presence of excess polystyrene sulfonic acid (PSS, free acid in 18% aqueous solution reagent) and a catalytic amount of iron sulphate. In a typical synthesis EDOT and polystyrene sulphonic acid were mixed in the ratios 1412 mg EDOT : 280 mg PSS : 178 mg APS. The reagents were added to milli-Q water (25 ml), purged with N_2 gas and the vessel sealed. The mixture was kept in an ice bath and stirred for 2 d. The resulting dark blue dispersion was diluted with milli-Q water to 50 ml and centrifuged at 4000 rpm for 30 min. The supernatant was then discarded, the solid resuspended in fresh milli-Q water, and centrifuged at 4000 rpm for 30 minutes to capture the solid. The supernatant was discarded and the process repeated twice. The solid was then diluted again to 50 ml and heated to 80°C for 1.5 h, after which it was cooled and centrifuged again. After discarding the supernatant, the solid was redispersed in a small volume of milli-Q water and freeze-dried to yield 0.323g of PEDOT-PSS (fluffy blue solid).

A spray coating solution was prepared by ultrasonic dispersion of the PEDOT-PSS at 0.1% weight concentration (corresponding to 1 mg / ml) in milli-Q water containing 5% ethylene glycol by weight, and mixed with **1** at 1:1 and 1:2 mass ratios, which corresponded to molar ratios of **1**: PEDOT-PSS of 1: 3.46 and 1 : 1.72. The resulting solutions were spray coated onto heated (70 ^{o}C) FTO glass using a low-cost commercial airbrush. The resulting coatings displayed a distinctive green colour that changed to blue when they were immersed in water. UV-visible measurements showed that the color change was due to the loss of **1** from the coatings during the immersion.

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2. S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, and C. B. Mullins, *Nano Lett.*, 2012, **12**, 26 .
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