# Autoxidation of polythiophene tethered to carbon cloth boosts its electrocatalytic activity towards durable water oxidation

Authors: Shi-Nan Zhang<sup>a</sup>, Zhong-Hua Xue<sup>a</sup>, Xiu Lin<sup>a</sup>, Yun-Xiao Lin<sup>a</sup>, Hui Su<sup>a</sup>, Shin-Ichi Hirano<sup>b</sup>, Xin-Hao Li<sup>a\*</sup> and Jie-Sheng Chen<sup>a</sup>

# Affiliations:

<sup>a</sup>School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China.

<sup>b</sup>Hirano Institute for Materials Innovation, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

Correspondence should be addressed to Xin-Hao Li; xinhaoli@sjtu.edu.cn

# **Supplementary Materials:**

- 1. Experimental Section
- 2. Figures S1 S16
- 3. Table S1
- 4. Reference S1 S5

#### 1.1 Oxidation of carbon cloth

The carbon cloth (CC) was ultrasonicated in 1 mol  $L^{-1}$  HNO<sub>3</sub>, ultra-pure water and ethanol for 5, 30 and 30 minutes respectively. The oxidized carbon cloth (or o-CC) was air-dried for further use.

#### 1.2 Preparation of PTh/CC and PTh/o-CC electrodes

The PTh/CC and PTh/o-CC electrodes were prepared with electrochemical polymerization method on the surface of CC and o-CC, respectively. The three-electrode system was made up of a work electrode, titanium mesh and a saturated calomel electrode (SCE), which were served as working electrode, counter electrode, and reference electrode, respectively. The acetonitrile electrolyte consisted of 0.005 mol L<sup>-1</sup> of thiophene and 0.1 mol L<sup>-1</sup> of supporting electrolyte (LiClO<sub>4</sub>). A constant potential of 1.73v vs. SCE was applied for 3 hours for PTh film synthesis without stirring. After synthesis, the electrodes soaked in ultra-pure water for 20min to remove the impurity.

## **1.3 Characterization**

UV-Vis spectra were recorded on a Shimadzu UV-2450 UV-Vis spectrophotometer. Attenuated total reflection-infrared (ATR-IR) spectra were collected on a Spectrum 100 spectrometer with a ATR-IR collector. Scanning electron microscopy (SEM) images were acquired on Nova NanoSEM 450 field emission scanning electron microscope (FEI, USA). Transmission electron microscopy (TEM) images were acquired on JEM-2100 microscope at an electron acceleration voltage of 200 kV. The samples were prepared by clamp a piece of coated carbon cloth fiber between two Cu grids. The X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos Axis Ultra DLD spectrometer using a monochromated Al Kα radiation.

#### **1.4 OER Electrochemical measurements**

OER performances were investigated using a CHI660E electrochemistry workstation (CH Instruments, Inc., Shanghai) in a standard three-electrode system. The three-electrode electrochemical cell was made up of a PTh electrode, a graphite rod and a saturated calomel electrode, which were served as working electrode, counter electrode, and reference electrode, respectively. All potentials were described versus the reversible hydrogen electrode (RHE) via the equation:  $E_{RHE} = E_{SCE} + 0.059 \text{ V} \times \text{pH} + 0.241 \text{ V}$ . Linear sweep voltammograms (LSV) measurements were conducted with a scan rate of 10 mV s<sup>-1</sup>. The OER performances were performed in solution with different pH values, 0.1 mol L<sup>-1</sup> KOH (pH =13), 1 mol L<sup>-1</sup> phosphate-buffered saline (pH =7), and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution (pH =0).

## 1.5 Electrochemical impedance spectroscopy

The EIS was performed in the frequency range from 1 MHz to 0.1 Hz at 1.7 V vs. RHE in 0.1 mol  $L^{-1}$  KOH solution. The semicircle in the Nyquist plots was fit with an equivalent circuit (inset in Figure 3e.)

## **1.6 Cyclic voltammetry test**

The standard three-electrode system was consisted with PTh electrode, Pt-net and SCE worked as working electrode, counter electrode and reference electrode respectively. The autoxidation process was studied in acetonitrile containing 0.1 mol  $L^{-1}$  NBu<sub>4</sub>BF<sub>4</sub> and 0.87 mol  $L^{-1}$  H<sub>2</sub>O. Different potential range were applied to study the autoxidation at a scan rate

of 20 mV s<sup>-1</sup>. All the initial potentials were -1.5 V vs SCE, while the highest potential of CV curves increased gradually.

## 1.7 Preparation of IrO<sub>2</sub> electrodes

5 mg IrO<sub>2</sub>, 350  $\mu$ L of H<sub>2</sub>O, 700  $\mu$ L of ethanol and 80  $\mu$ L of 5 wt % Nafion solution in alcohol were mixed and sonicated for 2 hours to form a homogeneous catalyst ink. 200  $\mu$ L ink was dropped on the carbon cloth (1 × 1 cm<sup>2</sup>, from CeTech, Taiwan.) and then dried at room temperature.

## **1.8** Computational methods

All theoretical calculations were performed using density functional theory (DFT), as implemented in the DMol3 program based on Materials Studio 8.0. The electronic exchange-correlation energy was described by the generalized gradient approximation (GGA) method with spin polarized Perdew-Burke-Ernzerhof (PBE) functional<sup>S1</sup>. Valence orbitals were described with the double numerical plus polarization (DNP) basis<sup>S2</sup>.

PTh and PTdO were modeled according to the XPS analysis results (Figure 3b and S14). Indeed, 60~80% of sulfur atoms on the surface of the polythiophene electrode were oxidized into sulfone groups.

In the calculation, the OER process are divided into four elementary reactions and each reaction only involves the transfer of an electron. The four rea ctions are shown below:

Step 1: H<sub>2</sub>O (l) + \*  $\rightarrow$  HO\* + H<sup>+</sup> + e<sup>-</sup> Step 2: HO\* + \*  $\rightarrow$  O\* + H<sup>+</sup> + e<sup>-</sup> Step 3: O\*+H<sub>2</sub>O (l) + \*  $\rightarrow$  HOO\* + H<sup>+</sup> + e<sup>-</sup> Step 4: HOO\*  $\rightarrow$  \* + O<sub>2</sub> (g) + H<sup>+</sup> + e<sup>-</sup>

where \* and  $X^*$  (X = HO, O, or HOO) represent a catalytic site and an adsorbed X intermediate on the polymer chain respectively.

The adsorption energies were calculated as follow:

$$\Delta E(OH^*) = E(OH^*) - E(^*) - [E(H_2O) - 1/2 E(H_2)]$$
  
$$\Delta E(OOH^*) = E(OOH^*) - E(^*) - [2E(H_2O) - 3/2 E(H_2)]$$
  
$$\Delta E(O^*) = E(O^*) - E(^*) - [E(H_2O) - 2 E(H_2)]$$

The Gibbs free energy change for adsorption was calculated as follow:

 $\Delta G_{\rm ads} = \Delta E_{\rm ads} + \Delta ZPE - T\Delta S$ 

The Gibbs free energy change of each step of OER was calculated as follow:

Step 1: 
$$\Delta G_1 = \Delta G(OH^*) - \Delta G(H_2O) - eU$$
  
Step 2:  $\Delta G_2 = \Delta G(O^*) - \Delta G(OH^*) - eU$   
Step 3:  $\Delta G_3 = \Delta G(OOH^*) - \Delta G(O^*) - eU$   
Step 4:  $\Delta G_4 = \Delta G(O_2) - \Delta G(OOH^*) - eU$ 

The overpotentials of OER could be determined using:

 $G^{\text{OER}} = \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \}$  $\eta^{\text{OER}} = G^{\text{OER}}/e - 1.23\text{V}$ 



**Figure S1.** SEM images of carbon cloths before (a) and after (b) HNO<sub>3</sub>-treatment. The smooth surface of the carbon cloth was not changed obviously after the mild oxidation process. The oxidized carbon cloth was used for further characterization and the fabrication of various electrodes. XPS (c) C 1s and (d) O 1s spectra of carbon cloths before and after HNO<sub>3</sub>-treatment. The increased amount of C-O groups as presented in both of the XPS (c) C 1s and (d) O 1s spectra of our mild HNO<sub>3</sub>-treatment method in introducing oxygen-based functional groups to the surface of carbon cloth for further depositing PTh polymer coating.



**Figure S2** Fourier transform infrared spectra of the bare carbon cloth and PTh electrode. The spectra indicates the successful deposition of thiophene-containing species on the surface of electrodes.



**Figure S3.** (a) Schematic structure of PTh electrode deposited on untreated carbon cloth. (b, c, d) SEM images of a PTh layer on as-received carbon cloth without  $HNO_3$  treatment. Large polymer aggregates were randomly deposited on the surface of carbon cloth. Large-scale continuous film of PTh layer was not observed.



**Figure S4.** (a) Schematic structure of PTh electrode deposited on  $HNO_3$ -treated carbon cloth. (b, c, d) SEM images of a PTh layer on  $HNO_3$ -treated carbon cloth. A homogeneous layer of PTh with a nanoscale roughness was observed, directly indicating the key importance of such a  $HNO_3$ -treatment process to the uniformity of PTh thin film deposited on the surface of carbon cloth.



**Figure S5**. SEM images of (a) fresh and (b) used PTh/o-CC electrodes. The stability of polymer films was further proved.



**Figure S6.** TEM images of PTdO electrodes using carbon cloth as the current collector. The electron-deposition time was tuned from (a) 0.5 h via (b) 3 h to (c) 5 h, generating PTdO layers with thicknesses of nearly 16, 26 and 78 nm, respectively, with respect to the calculated polymer components volumes of  $1.6 \times 10^6$ ,  $2.6 \times 10^6$  and  $7.8 \times 10^6 \,\mu\text{m}^3 \,\text{cm}^{-2}$  of per unit electrodes. The linear sweep voltammograms of PTdO electrodes with various thickness measured in a 0.1 mol L<sup>-1</sup> KOH solution (pH = 13) with a scan rate of 10 mV s<sup>-1</sup> (d) before and (e) after iR-correction.



**Figure S7**. EIS Nyquist plots of PTdO/o-CC electrodes with different thickness. The increased thickness of the PTh films generate an even higher intrinsic resistance of the electrodes as estimated from their EIS plots



**Figure S8.** The LSV curves of PTdO, PTh,  $IrO_2$  and bare carbon cloth electrodes measured in 0.1 mol L<sup>-1</sup> KOH solution (a) before and (b) after iR-correction.



**Figure S9.** (a) Cyclic voltammetry curves of PTdO/o-CC electrode under a scan rate of 100 mV s<sup>-1</sup>(green), 50 mV s<sup>-1</sup>(blue). 10 mV s<sup>-1</sup>(red) .2 mV s<sup>-1</sup>(black). (b) Enlarged view of the dashed part in (a). Detailed CV curves at different scan rates indicated a very narrow window of the capacitive behavior and thus a negeligible effect of a rate of 10 mV s<sup>-1</sup>.



**Figure S10.** Cyclic voltammetry curves of PTh electrode at the same potential range for successive three times, indicating the fast autoxidation process of the thiophene rings.



**Figure S11** (a) Chronoamperometric stability measurement of PTh/o-CC and bare o-CC electrodes in 0.1 mol  $L^{-1}$  KOH solution under 1.7 V vs. RHE. (b) LSV curves of PTdO/o-CC, fresh and used o-CC electrodes measured in 0.1 mol  $L^{-1}$  KOH solution. The constant current output in the i-t curve of o-CC electrode with nearly the same LSV curves after a ten-hour test exclude the possible contribution of oxidation of carbon cloth on the improved OER performance.



**Figure S12**. Photographs of o-CC, PTh/o-CC and PTdO/o-CC electrodes before and after the drop of water. All electrodes used in this work are hydrophilic, excluding the possible effect of surface wettability to the varied OER activity of PTdO electrode in this work.



**Figure S13.** Chronoamperometric stability measurement of PTh/o-CC electrodes at 2 V vs. RHE in (a) 0.1 mol L<sup>-1</sup> KOH, (b) 1 mol L<sup>-1</sup> phosphate-buffered saline, and (c) 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, respectively. The PTdO/o-CC electrode provided a constant current output even at a current density of 45 mA cm<sup>-2</sup> in 0.1M KOH.



**Figure S14.** CDD stereograms after the adsorption of OOH onto the PTh model. As compared with the CDD stereogram of the PTdO-based model, the charge exchange and the interaction between the OOH specie and the PTh are weaker.



**Figure S15.** (a) PTh and (c) PTdO models for DFT calculation. Optimized absorption structures (top and side view) of each step of OER process on (b) PTh and (d) PTdO models.



**Figure S16.** XPS S 2p spectra of used PTdO electrodes for 3h and 17h during the i-t test at the potential of 1.7 V vs. RHE in 0.1M KOH. The chemical structure of the oxidized polymer was not changed obviously, rather speaking for the acceptable OER stability of PTdO electrode.

Catalysts	Overpotential (mV) for OER at 10 mA cm <sup>-2</sup>	Current density (mA cm <sub>-2</sub> ) at 1.7 V vs. RHE	Tafel slope (mV dec <sup>-1</sup> )	рН	Ref.
PTdO	430	23.8	61	13	This work
p-FGDY	460	11	128	14	14
PPPI	470	9.1	75	13	15
g-C3N4	749	~2	120.9	13	S3
g-C3N4/ graphene	539	~7	68.5	13	S3
PCN-CFP	400	~30	61.6	13	S4
GO- PANi-FP	570	5	141	13	S5

**Table S1.** Comparison of OER catalytic performance for metal-free organicelectrocatalysts.

# Reference

- [S1] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, 77, 3865-3868.
- [S2] B. Delley, J. Chem. Phys. 1990, 92, 508-517.

[S3] J. Tian, Q. Liu, A. M. Asiri, K. A. Alamry and X. Sun, *ChemSusChem*, 2014, 7, 2125-2130.

[S4] T. Y. Ma, J. Ran, S. Dai, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.* 2015, **54**, 4646-4650.

[S5] J. Zhang and L. Dai, Angew. Chem. Int. Ed. 2016, 55, 13296-13300.