Supporting Information

Immobilization of a Molecular Catalyst on Carbon Nanotubes for Highly Efficient Electrocatalytic Water Oxidation

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General Methods, Experimental Section and Instrument Details.

Materials and Instrumentation

All chemicals and solvents, if not stated, were purchased from Sigma Aldrich without further purification; water used in syntheses and measurements was deionized by Milli-Q technique. 4-hydroxy-2,6-pyridinedicarboxylic acid, 4-methylpyridine and 1-dodecanol were purchased from TCI. MWCNTs-COOH and MWCNTs were purchased from Nanocyl. cis-Ru(DMSO)$_4$Cl$_2$ was prepared as described previously[1]. Complex Ru-C12 was synthesized and fully characterized by NMR, mass spectrometry and elemental analysis (supporting information). NMR spectra were recorded by Bruker Advance 500 spectrometer. Mass spectrometry was performed on a Finnigan LCQ Advantage MAX mass spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 apparatus. IR were performed with Thermo Nicolet iS50 FT-IR.

Electrochemical measurement.

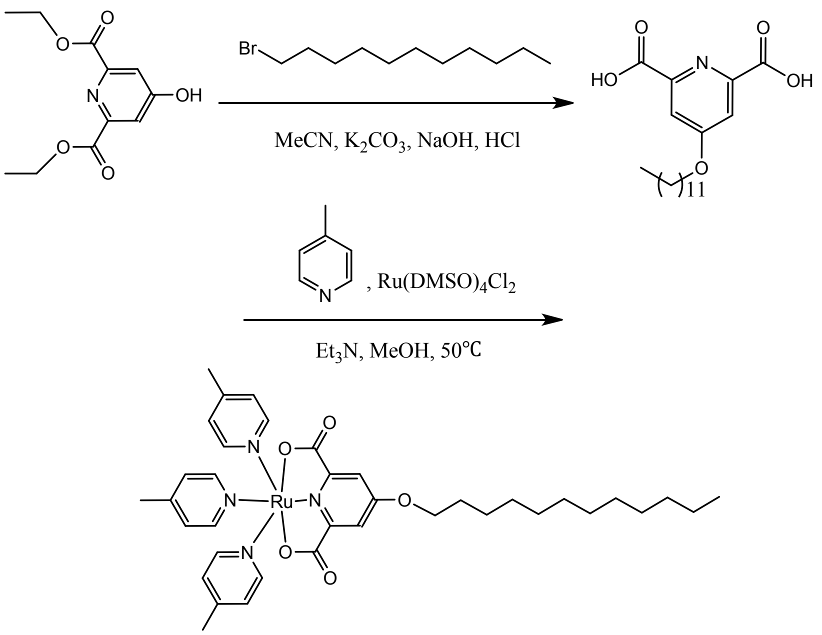
All electrochemical measurements were carried out in a three-electrode system using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). A platinum foil was employed as the counter electrode. Glassy carbon (GC) disk electrodes (3 mm diameter) were employed as working electrodes, which were polished successively by 50 nm aluminum oxide particles on cloth polishing pads and then washed in ethanol under ultrasonication. Immobilized catalyst-CNTs@GDL(gas diffusion layer) on rotating disk electrode was employed as working electrode too. A Ag/AgCl in 3 M KCl was employed as the reference electrode, $E_{1/2}$ was determined by taking the average of the anodic and cathodic peak potentials ($E_{1/2}=(E_{pa}+E_{pc})/2$) from the cyclic voltammetry. All potentials were converted to the NHE by using $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ couple (Half-wave potential $E_{1/2}=1.26$ V vs. NHE) as an external reference, when needed.

Faradaic efficiency. For bulk electrolysis experiments, a tight cell was used. The cell was degassed by N_2 for 20 min before electrolysis. The electrolysis current was recorded with controlled-potential of 1.3 V vs. NHE on the working electrode for 1 h and 15 h in 50 mM phosphate buffer (pH 7.0, IS=0.1).

Determination of O_2 generation. In the end of the experiment, the volume of the solution and the headspace in the working compartment were measured. To evaluate real oxygen generation, 0.5 mL of the headspace of the system was transferred into a gas chromatography (GC) using a Hamilton SampleLock syringe. GC-2014, Shimadzu (Molecular sieve 5A, TCD detector, nitrogen as a carry gas) was used to confirm the oxygen evolution, with the helium as a carry gas.

Scanning electron microscopy (SEM). A SEM ZEISS Ultra 55 on connection to an OXFORD INSTRUMENTS INCA Energy EDS System was used for SEM and EDS. The acceleration voltage was 7 kV. All samples were rinsed with deionized water and dried by air before loading into the instrument.

Preparation of compounds



Scheme S1. Synthesis Procedures

Diethyl 4-hydroxypyridine-2,6-dicarboxylate

The synthesis was adapted from that described[2]. Chelidamic acid (5 g, 27.3 mmol) was suspended in absolute ethanol (100 mL) and sulfuric acid (97%) was carefully added at room temperature with vigorous stirring. The yellow mixture was refluxed for 4 h and the solvents evaporated. Water (100 mL) was then added and the solvent was evaporated again. The viscous residue was neutralized with a saturated solution of $NaHCO_3$ to pH 8 and the aqueous solution was extracted with CH_2Cl_2 (800 mL). The organic phase was dried with Na_2SO_4 and evaporated to give product as a pale solid (6.2 g, 95%).

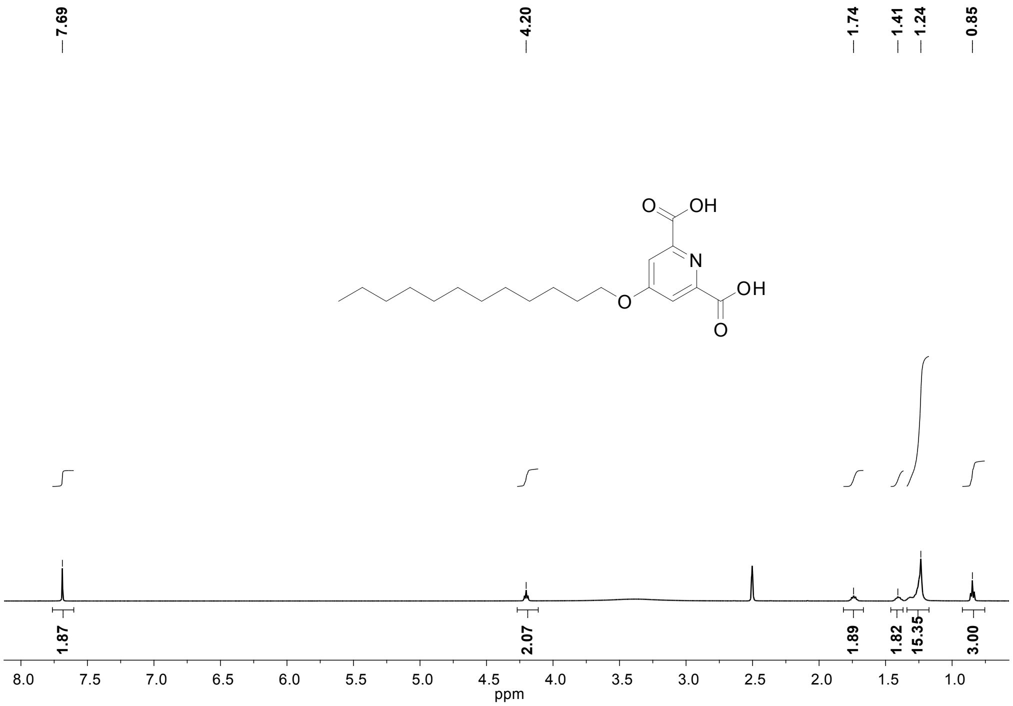
4-(dodecyloxy) pyridine-2, 6-dicarboxylicacid

Diethyl 4-hydroxypyridine-2,6-dicarboxylate(2.4 g, 1mmol) and 1-bromododecane(3g, 1.2mmol) were dissolved in MeCN(20ml) , K_2CO_3(2.0g, 1.5mmol) and KI (0.16g, 0.1mmol) were added. The solution was refluxed for 12h and the solvents evaporated, water (100 mL) was added and the aqueous solution was extracted with CH_2Cl_2 (500 mL). After evaporation of the CH_2Cl_2, MeOH 50mL, water 10mL and KOH 3g were added. The reaction mixture was stirred for 18 h at room temperature and was then poured into a mixture of ice and conc. HCl. A white solid precipitated, which after filtration and drying gave the product (2.5g, 72%).^{1}H-NMR (500 MHz, d^6-DMSO): 0.85 (t, 3H), 1.24 (s, 16H), 1.41 (m, 2H), 1.74 (m, 2H), 4.20 (t, 2H) 7.69 (s, 2H); ^{13}C-NMR (500 MHz, d^6-DMSO): 12.79, 22.18, 25.18, 25.19, 29.06, 31.25, 68.96, 113.55, 149.94, 165.27, 166.79. MS (ESI): calcd for 350.44 ($M + H^+$), found $m/z^- = 350.56$.

Ru-C12 :

242 mg (0.5 mmol) $Ru(DMSO)_4Cl_2$, 176 mg (0.5 mmol)4-(dodecyloxy)pyridine-2,6-dicarboxylic and 500 µl NEt_3 were dissolved in 25 mL MeOH. The mixture was degassed by N_2 and heated at 50 °C for 4 h, 1 mL 4-picoline was added to the mixture and then the reaction was kept refluxing overnight under the protection of N_2. After cooling down, solvent of the reaction mixture was removed by rotating evaporator and the remaining solid was dissolved in CH_2Cl_2 (15 ml) and washed with water (10 ml × 3) to remove organic salt. The organic layer was dried over anhydrous Na_2SO_4 and CH_2Cl_2 was removed by rotary evaporating. The raw product was purified by column chromatography over silica (2% methanol in toluene), complex **Ru-C12** was afforded as a dark-brown solid (240 mg, 66 % yield). ^{1}H-NMR (500 MHz, d^4-methanol): 0.86 (t, J = 10, 3H), 1.24 (s, 16H), 1.44 (m, 2H), 1.80 (m, 2H), 2.25 (s, 6H), 2.36 (s, 3H), 4.14 (t, J = 5, 2H), 7.03(d, J = 10, 4H), 7.23(d, J = 5, 2H) 7.59(s, 2H) 7.93(d, J = 5, 4H), 8.59(d, J = 5, 2H); ^{13}C-

NMR (500 MHz, d^4-methanol):1.48, 14.34, 20.64, 23.63, 27.00, 29.64, 30.65, 32.97, 70.64, 115.66, 126.62, 127.08, 149.44, 153.61, 165.29, 171.60; IR: *v* = 2921 cm^{-1}, 2851 cm^{-1}, 1631 cm^{-1}, 1601 cm^{-1}, 1422 cm^{-1}, 1322 cm^{-1}, 1101 cm^{-1}, 1003 cm^{-1}, 918 cm^{-1}, 880 cm^{-1}, 819 cm^{-1}, 736 cm^{-1}; HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{37}H_{48}N_4O_5Ru$, 730.2659; found, 730.2701. Anal. calcd for $C_{37}H_{48}N_4O_5Ru$: C 60.89, H 6.63, N 7.68; found: C 60.27, H 6.46, N 7.20.



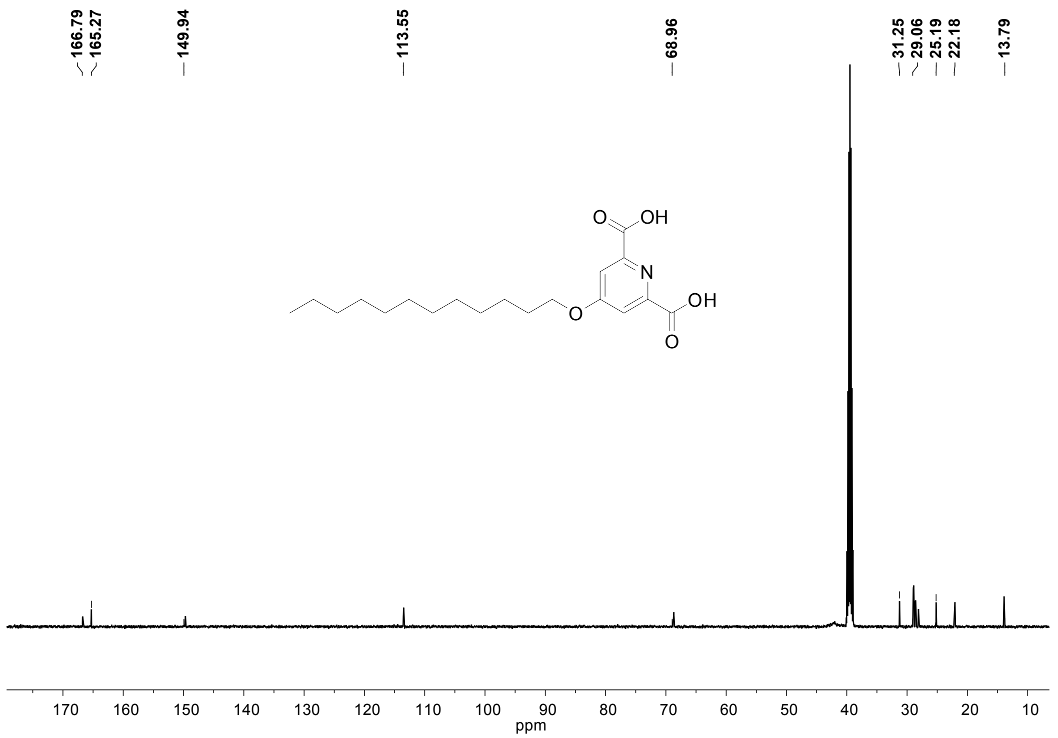
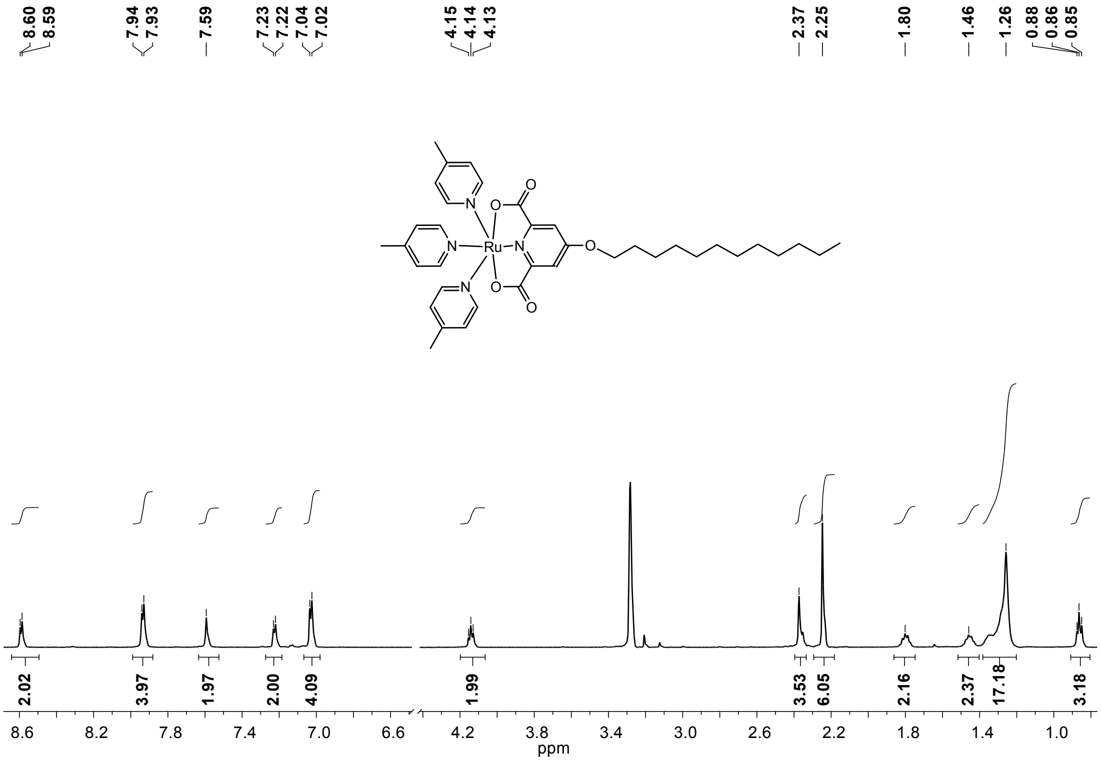


Figure S1. ^{1}H NMR and ^{13}C NMR of **4-(dodecyloxy) pyridine-2, 6-dicarboxylicacid**



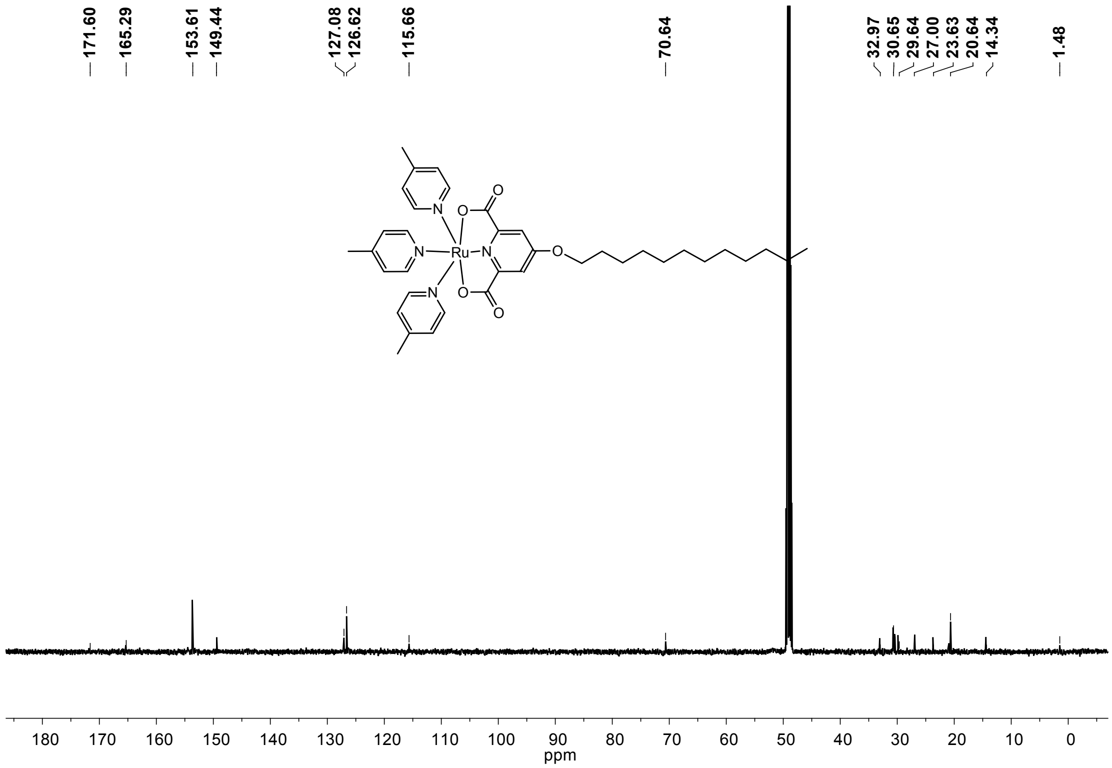


Figure S2. ^{1}H NMR and ^{13}C NMR of **Ru-C12**

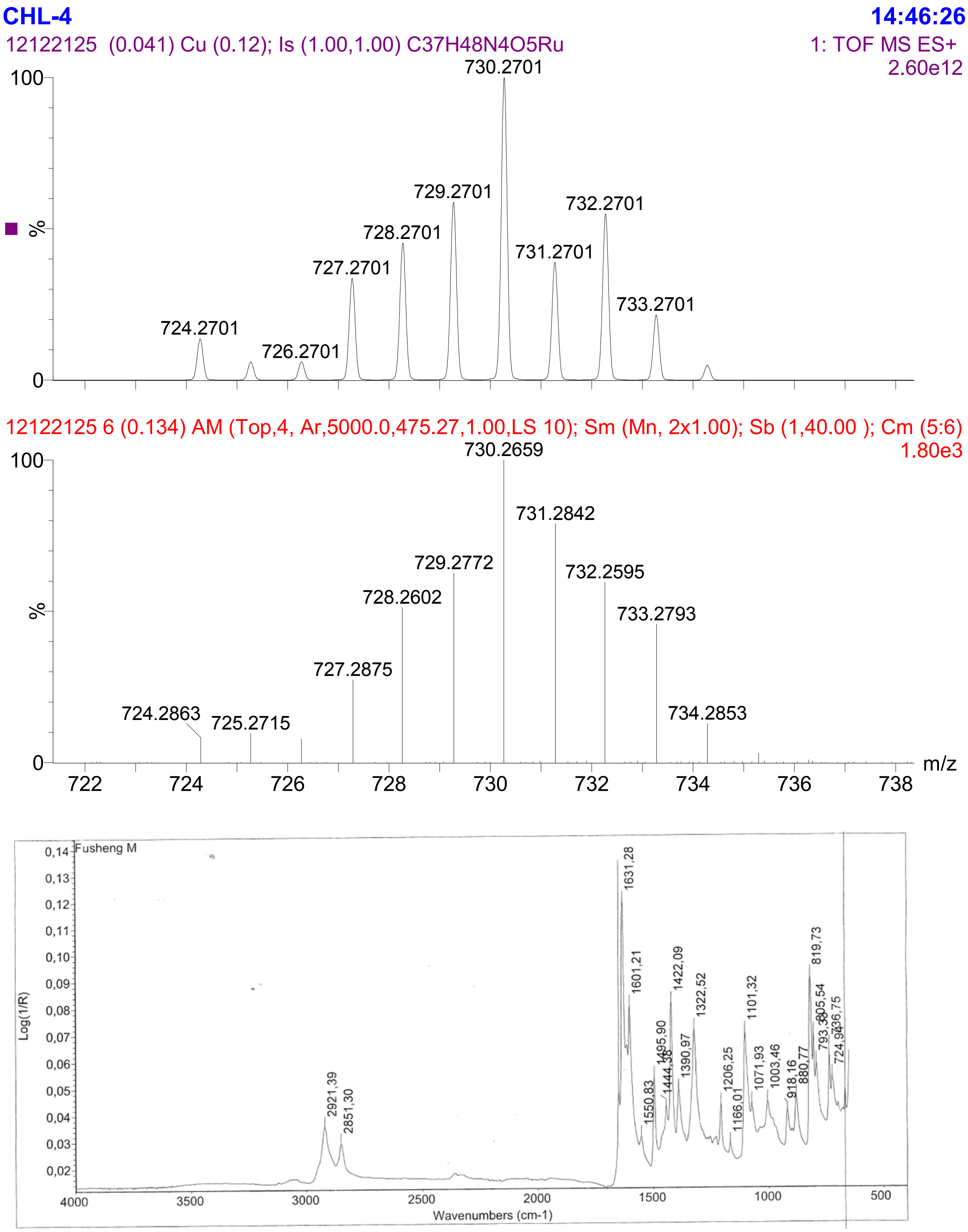


Figure S3. MS and IR of **Ru-C12**

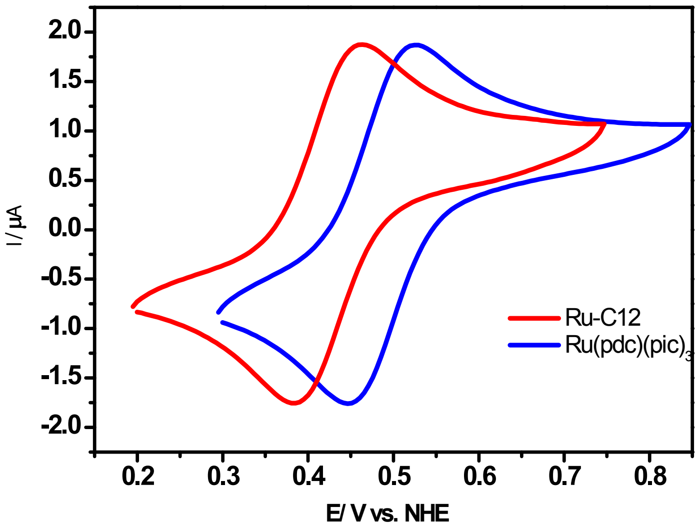


Figure S4. Cyclic voltammograms (CV) of Ru-C12 (1mM, red line) and Ru(pdc)(pic)$_3$ (1mM, blue line), in 0.1 M $nBt_4N^+PF_6^-$ solution of DCM with glass carbon as the working electrode, Ag/AgNO$_3$ as the reference electrode, and Pt as the counter electrode. Scan rate is 100 mV s^{-1}.

Immobilization of Ru-C12 on CNTs

The solution of **Ru-C12** (3.65mg, 0.005mmol) in Trifluoroethanol (5 mL) was added into the solution of MWCNTs (3mg) dispersed in water (200ml), and ultrasonicated for 15 minutes. The same method was used to prepare **Ru-C12-MWCNTsCOOH** using MWCNTsCOOH instaed.

Immobilization of Ru-C12-MWCNTs@GDL.

The suspension of **Ru-C12@** MWCNTs was deposited by filtration onto the Gas Diffusion Layer support (d = 4.4 cm, S =15 cm2) yielding electrodes with MWCNTs charge of 0.2 mg cm^{-2} and **Ru-C12** charge of 0.24 mg cm^{-2}. The electrode was vacuum dried for 12h.

Immobilization Ru-C12-MWCNTsCOOH@GDL.

The suspension of **Ru-C12**@MWCNTsCOOH deposited by filtration onto the Gas Diffusion Layer support (d = 4.4 cm, S =15 cm^2) yielding electrodes with **MWCNTsCOOH** charge of 0.2 mg cm^{-2} and **Ru-C12** charge of 0.24 mg cm^{-2}. The electrode was vacuum dried for 12h.

Immobilization of Ru(pdc)(pic)$_3$–MWCNTsCOOH@GDL.

The same method described above was used to immobilize **Ru(pdc)(pic)$_3$–MWCNTsCOOH@GDL,** yielding electrodes with MWCNTsCOOH charge of 0.2 mg cm^{-2} and **Ru(pdc)(pic)$_3$** charge of 0.2 mg cm^{-2}

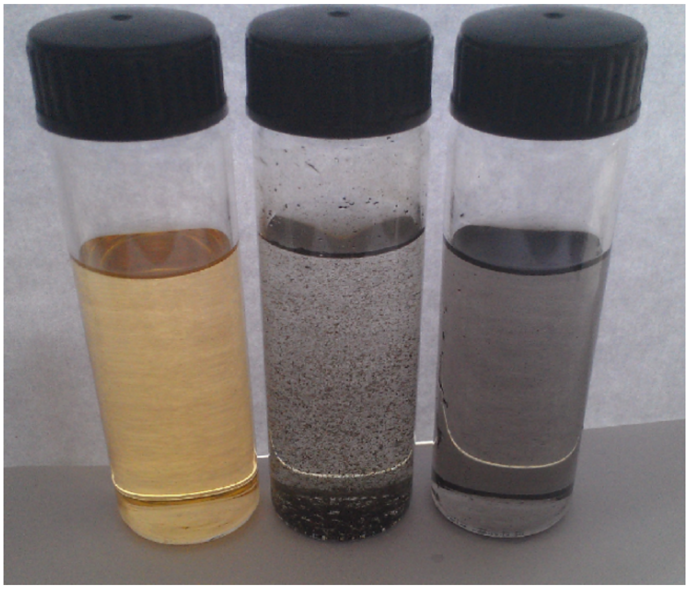


Figure S5. The solution of **Ru-C12** (0.37 mg, 0.0005 mmol) in 10mL water containing 20% trifluoroethanol (left).

MWCNTs-COOH (0.15mg) dispersed in 10ml water containing 20% trifluoroethanol (right), and a mixed solution of Ru-C12 (0.37 mg, 0.0005 mmol) and MWCNTs-COOH (0.15 mg) in 10mL water containing 20% trifluoroethanol (mid)

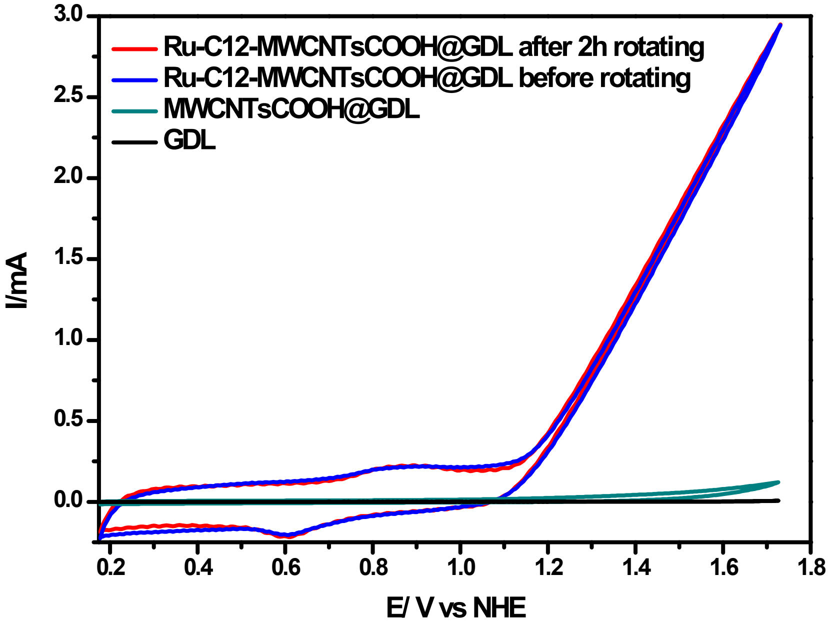


Figure S6. Cyclic voltammograms (CVs) of **[Ru-C12-MWCNTsCOOH@GDL]** electrode (blue), **[Ru-C12-MWCNTsCOOH@GDL]** electrode after rotated for 2h (red), without catalyst only **MWCNTs@GDL** (green), blank only GDL (black). All the CVs were carried out using rotating disk electrode (1000 rpm, 0.2 cm^2) as working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode, in aqueous solution (phosphate buffer, pH=7.0, ionic strength=0.1). Scan rate is 100 mVs^{-1}.

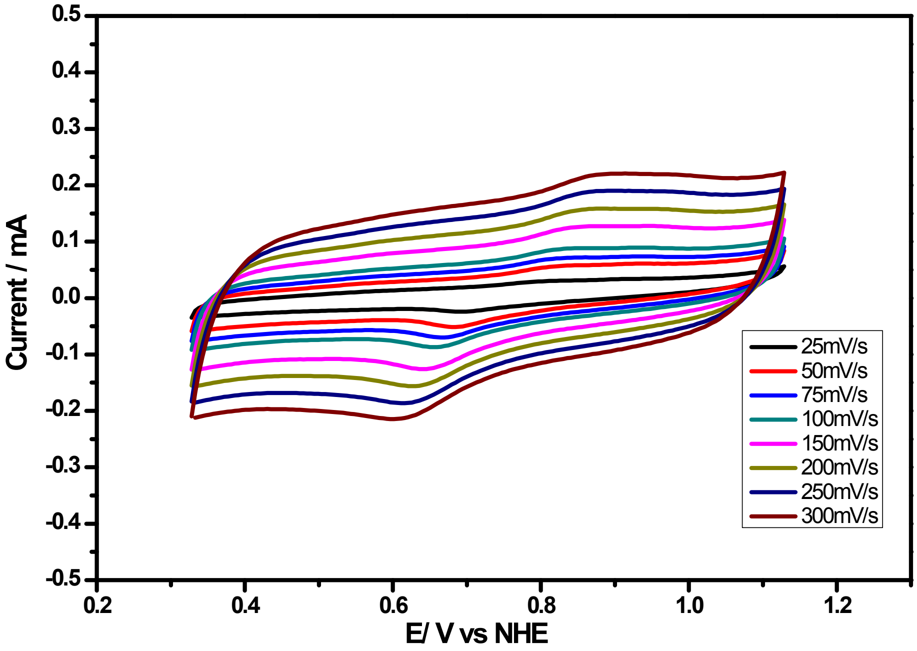


Figure S7: CV curves of [**Ru-C12**-MWCNTs@GDL] electrode at different scan rates.

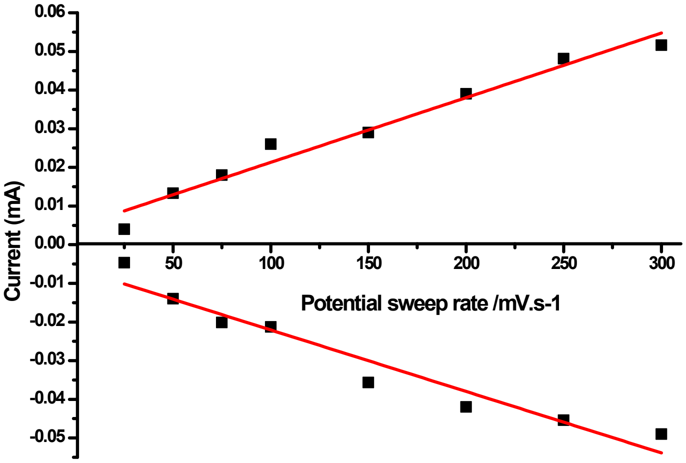


Figure S8: dependence of peak current on different scan rates for (RuII/RuIII) = 0.85 V vs. NHE and (RuIII/RuII) = 0.6 V vs. NHE.

$$\text{slope} = \frac{\mathrm{n}^2 F^2 A \Gamma_0}{4\mathrm{RT}} \qquad (1)$$

T = room temperature, F = Faraday's constant = 96485, n = number of electrons = 1, R = ideal gas constant = 8.314 $JK^{-1}mol^{-1}$, T = temperature = 298 K, A = electrode surface area (cm^2), Γ_0= surface concentration (mol/cm^2), peak current (A), scan rate (V/s).

$$TOF = \frac{1}{4} \times \frac{1}{t} \times \frac{Q}{F\Gamma_0} \tag{2}$$

Assuming the Faraday efficiency is 100%, and F is Faraday constant, Q is the integrated charge through the electrode (background is subtracted), Γ_0 is working catalyst amount 8.5 ± 0.4 (10^{-10} mol cm^{-2}), t is integration time (60 s), and generation of each O_2 molecule includes extraction of four electrons from two H_2O molecules.

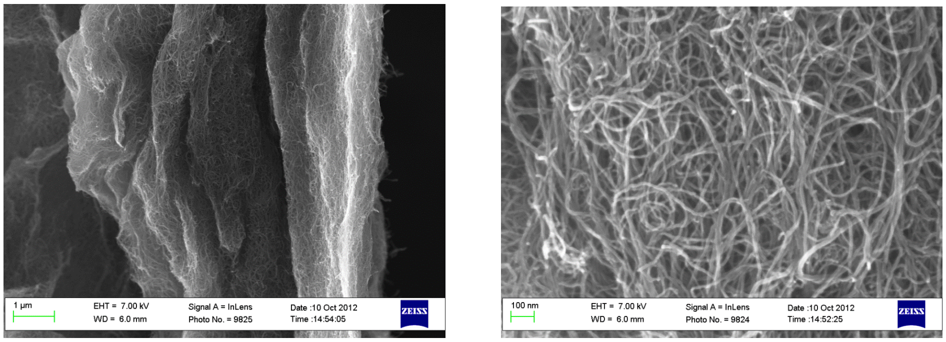


Figure S9. SEM images of MWCNTsCOOH@GDL electrode

Element	Weight % Sigma	Atomic %
C K	1.03	93.03
O K	0.47	3.32
F K	0.36	2.26
Ca K	0.53	1.35
Ru L	0.83	0.04
Totals	100	

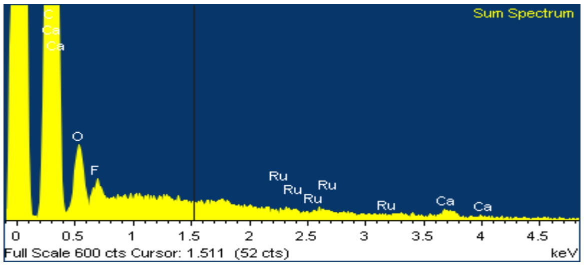


Table S1 and **Figure S10.** EDX analysis of MWCNTsCOOH@GDL electrode.

The surface was uniform, with cracks and smooth areas. The EDX was done on the small area shown in the top figure. The Ru content is below the uncertainty in the measurement; i.e. there is no Ru.

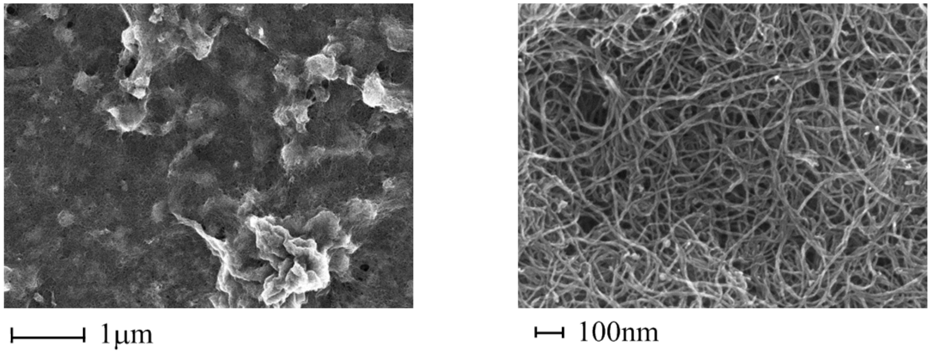


Figure S11. SEM images of **Ru-C12-MWCNTsCOOH@GDL** electrode

Element	Weight %	Atomic %
C K	73.08	82.50
O K	1.32	1.12
F K	22.34	15.94
Ru L	3.26	0.44
Totals	100.00	

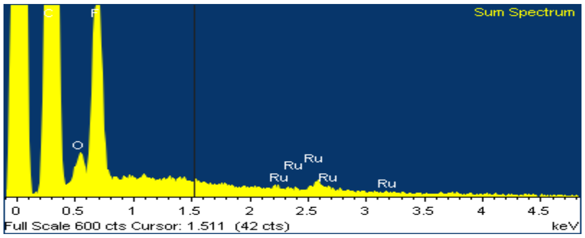


Table S2 and **Figure S12.** EDX analysis of **Ru-C12-MWCNTsCOOH@GDL** electrode.

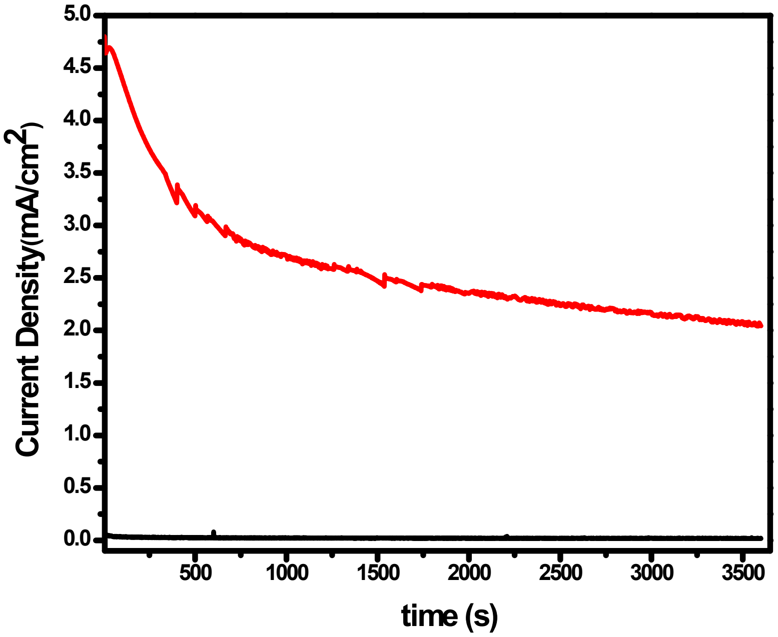
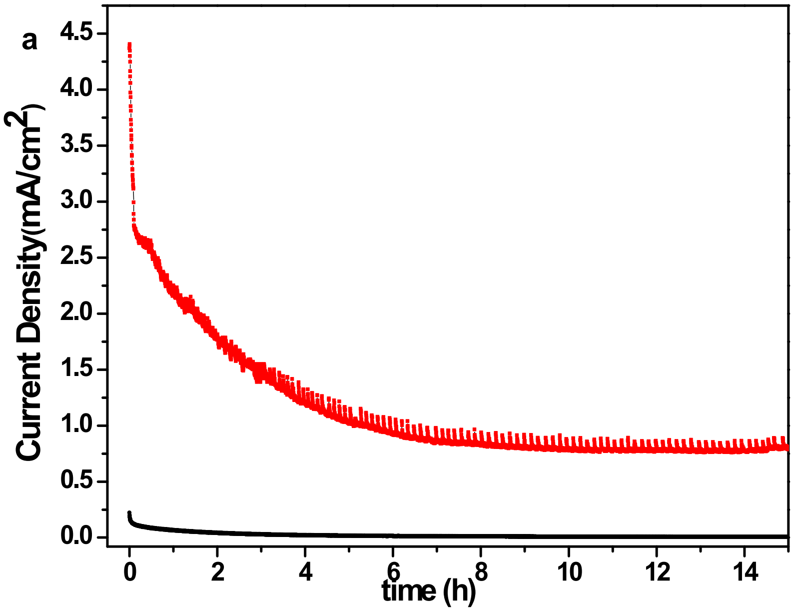


Figure S13. Electrolysis of **Ru-C12-MWCNTsCOOH@GDL** electrode at 1.3V (vs. NHE) applied potential in 50mM phosphate buffer, pH = 7.0 electrolyte for 1 h (red trace) and **MWCNTsCOOH@GDL** electrode background (black trace).



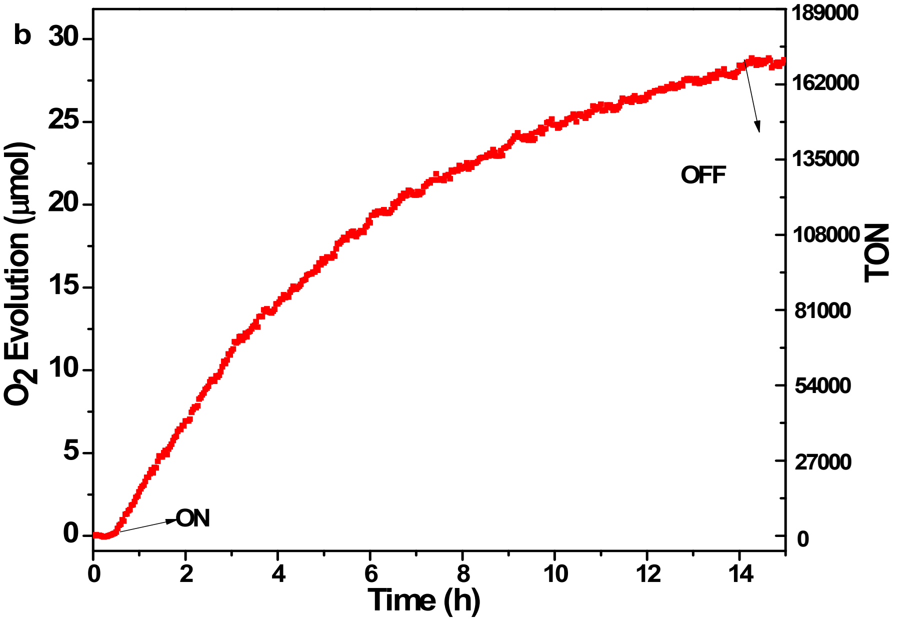


Figure S14. a: Current density of Ru-C12-MWCNTsCOOH@GDL electrode (red trace) and MWCNTsCOOH@GDL electrode (black trace) for bulk electrolysis experiment (50 mM potassium phosphate buffer pH 7.0 with controlled potential 1.3 V vs. NHE for 15 hours. Ag/AgCl as the reference electrode, and Pt as the counter electrode).
b: The amount of oxygen and TON measured by oxygen sensor and GC.

Table S3: The performance of different anode electrodes for electro-catalytic water oxidation from our work and in comparison with some literature reported ones.

	Applied potential [V vs.NHE]	pH	Current density [$mAcm^{-2}$]	Faraday efficiency	TON	TOF	TOFb)
This work 1h electrolysis	1.3	7.0	2.2	96%	27 647	7.6a)	12.4
This work 15h electrolysis	1.3	7.0	0.84	93%	170 588	3.5a)	
ITO\MWCNT\Ru(bda)(Py-pyrene)$_2$ 20h[3]	1.4	7.0	0.22	96%	11 000	0.3	
ITO\MWCNT\polyoxometalate cluster[4]	1.42	7.0	≈0.2	-	-	-	0.085
ITO\redox mediator assembly with Mebimpy 13h[5-7]	1.8	1.0	-	>95 %	28 000	0.6	
ITO\redox mediator assembly with tpy 13h[5-7]	1.8	1.0	0.0067	>95 %	8900	0.3	

a) Average TOF in electrolysis experiments for 1h and 15h; b) TOF in chronoamperometric experiments which means initial TOF.

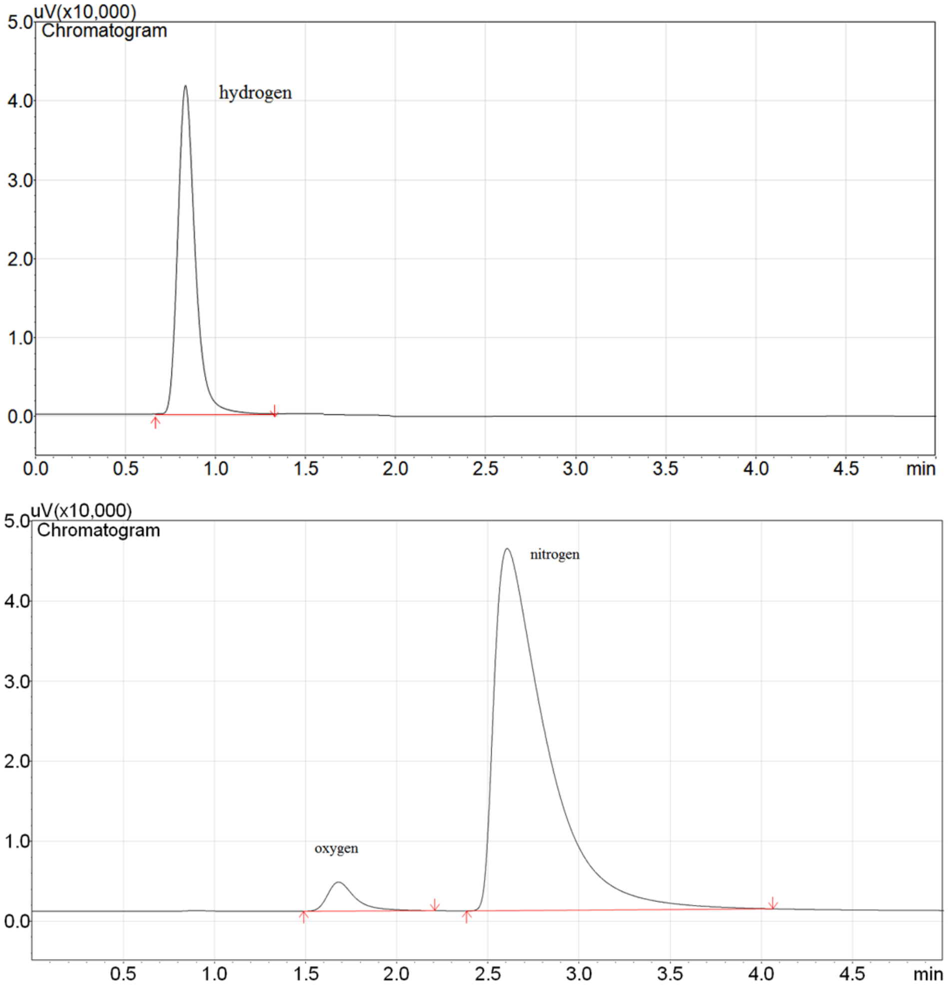


Figure S15. Hydrogen and oxygen detected by GC (hydrogen 61.7 μmol, oxygen 29.0 μmol) for 15h electrolysis. Helium and nitrogen as carry gases.

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