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Highly Efficient Heterogeneous Water Oxidation of Ru^{II} Disulfonic Acid Terpyridine Complex on Carbon Nanotubes via π-π Interactions

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MATERIALS

General Procedures

All chemicals and reagents were purchased from commercial suppliers (Shanghai Macklin Biochemical Technology Co., Ltd. and Shanghai Titan Scientific Co., Ltd.) and used as received. Multi-Walled Carbon Nanotubes (MWCNTs) used in this work were in bulk with >95% purity, >20 nm OD and ~1 μm length. High-purity deionized water was obtained by passing distilled water through a nanopure Milli-Q water purification system. All synthetic manipulations were routinely performed under Ar atmosphere using vacuum-line techniques.

METHODS AND INSTRUMENTATION

General instrumentation

Electrospray ionization mass spectrometry (ESI-MS) was performed with a Thermo Scientific Q Exactive Mass Spectrometer. A 400 MHz Bruker Avance II spectrometer was used to carry out NMR spectroscopy at room temperature unless otherwise specified. FTIR spectra were obtained by using a Thermofisher Nicolet 50 spectrometer. UV-Vis spectroscopy was performed on a HITACHI UV-Visible/NIR UH4150 spectrophotometer.

Electrochemical methods

All the Electrochemical measurements were performed with a CH Instruments CHI-760E bipotentiostat at ambient temperature with a glassy carbon disk (GC, ϕ = 3 mm, S = 0.07 cm^2) working electrode, platinum wire counter electrode, and Ag/AgCl (KCl sat.) reference electrode unless indicated and potentials were converted to NHE by adding 0.2 V.

Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV) and Linear Sweep Voltammetry (LSV)

For electrochemical study, a 30 mL vial was used as an electrochemical cell. Cyclic Voltammograms (CV) were recorded at 100 $mV \cdot s^{-1}$ scan rate, unless explicitly expressed. The DPV parameters were ΔE = 4 mV, Amplitude = 50 mV, Pulse width = 0.05 s, Sampling width = 0.0167 s, Pulse period = 0.5 s unless explicated. LSV performed with 85% iR compensation.

Bulk electrolysis

For bulk electrolysis experiments, a 30 mL vial was used as an electrochemical cell. In the case of the oxygen-monitored bulk electrolysis, a 20 mL two-compartment cell with a separation membrane between the two compartments was used. Both compartments were filled with 10 mL of pH = 7 solution and both compartments were equipped with a stirring bar. A Clark electrode was used to measure oxygen evolution and to calculate the Faradaic efficiency (FE). Eq. S1 was used to calculate the FE, n is the moles of the O_2, F is the Faraday constant, Q is the total charge generated during the electrolysis.

$$FE = 4nF/Q \quad \text{(S1)}$$

Surface coverage (Γ)

The surface coverage (Γ) of the complexes on the electrodes was estimated by applying the Eq. S2, where Q is the average charge under the Ru^{III}/Ru^{II} oxidation and reduction wave in CV, n is the number of electrons involved in the electron transfer (n = 1), S is the surface of the electrode (GC, S = 0.07 cm^2) and F is the Faradaic constant (96485 C). The average coverage was estimated from 3 independent experiments and the standard deviation between samples was used as an error.

$$\Gamma = Q/nFA \quad \text{(S2)}$$

Preparation of {Ru(tds)$(L)_2$}@MWCNT@GC electrode

Dispersion and Mixing: 1 mg of MWCNT was dispersed in 1 mL of 2,2,2-trifluoroethanol (TFE) via sonication. Separately, 1 mg of Ru(tds)$(L)_2$ was dissolved in 1 mL of dimethyl sulfoxide (DMSO). Then, 150 µL of the catalyst/DMSO solution was added to the MWCNT/TFE suspension and mixed thoroughly to allow adsorption via

π-π interactions.

Purification: The mixture was poured into 20 mL of anhydrous ethanol to co-precipitate the {Ru(tds)$(L)_2$}@MWCNT. The product was collected by centrifugation (7000 rpm, 5 min), and the supernatant was discarded. This washing step with ethanol was repeated several times until the supernatant became colorless and clear, ensuring the removal of unbound (physically adsorbed) catalyst molecules. This rigorous purification is crucial for attributing the electrochemical response primarily to strongly anchored catalysts.

Electrode Fabrication: The final purified hybrid was re-dispersed in 0.5 mL of anhydrous ethanol. A measured volume of this ink was drop-cast onto a polished glassy carbon (GC) electrode and dried in air, yielding the {Ru(tds)$(L)_2$}@MWCNT@GC working electrode.

Electrochemical Solutions

All solutions used in this work possessed an ionic strength equal to 0.1 M. Phosphate buffer solution (PBS, pH = 2) was prepared by mixing H_3PO_4 (0.1073 mol) and NaH_2PO_4 (0.0986 mol) in 1000 mL of Milli-Q water. PBS (pH = 7) was prepared by mixing NaH_2PO_4 (0.0193 mol) and Na_2HPO_4 (0.0266 mol) in 1000 mL of Milli-Q water. PBS (pH = 11.6) was prepared by mixing Na_2HPO_4 (0.0073 mol) and Na_3PO_4 (0.0126 mol) in 1000 mL of Milli-Q water[1]. Solutions at pHs between 2.0 and 11.6 were prepared by mixing the above solutions. The pHs of all solutions were measured by a pH meter.

Foot of the wave analysis (FOWA)

Catalytic rate constants for the water oxidation, k_{obs}, were calculated using Eq. S3, where i is the catalytic current taken at 1.6 V, Q_R is the average charge detected by the CV, F is the Faraday constant, E^0 is the redox potential of the active species (Ru^{III}-OH)/(Ru^{II}-OH_2), E is the applied potential, R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), and T is the absolute temperature (293.15 K).

$$\frac{i}{Q_R} = \frac{k_{obs}}{1 + exp\left(\frac{F(E - E^0)}{RT}\right)} \quad \text{(S3)}$$

Single-crystal X-Ray Diffraction (XRD) Methods

Single crystal of $Ru^{II}(tds)(L)_2$ was obtained by slow diffusion of diethyl ether into a DMSO solution of $Ru^{II}(tds)(L)_2$ at room temperature. The diffraction data of $Ru^{II}(tds)(L)_2$ was measured at 296 K by using Cu Kα radiation (λ = 1.54178 Å) on a 'Bruker APEX-II CCD' diffractometer. The crystal structure was solved with the Olex2. structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table S1.

Table S1 Summary of the crystallographic data for $Ru^{II}(tds)(L)_2$

	$Ru^{II}(tds)(L)_2$
Empirical formula	$C_{57}H_{35}N_5O_6RuS_2$
Formula weight	1051.11
Temperature/K	296
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.8348(9)
b/Å	18.1857(9)
c/Å	19.1515(9)
α/°	90
β/°	114.546(3)
γ/°	90

Volume/Å^3	5333.4(5)
Z	4
ρ_{calc}g/cm^3	1.505
μ/mm^{-1}	4.364
F(000)	2484.0
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.026 to 80.102
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	33303
Independent reflections	3231 [R_{int} = 0.0721, R_{sigma} = 0.0344]
Data/restraints/parameters	3231/9/720
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1265
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1333

Synthesis of ligands and complexes

6,6"-disulfonic acid-[2,2':6',2"-terpyridine](H_2tds) and 4-(pyrene-1-yl)pyridine (L) were prepared according to literature procedures[2, 3]. Powder sample of Catalyst Ru(tds)$(L)_2$ was prepared similarly as previously described[2].

6,6"-disulfonic acid-[2,2':6',2"-terpyridine](H_2tds). A mixture of 6,6"-dibromo-2,2':6',2"-terpyridine (500 mg, 1.28 mmol) and sodium hydrosulfide (730 mg, 13 mmol) in 15 mL DMF was heated at 140 ℃ for 12 hours under Ar. Deep green mixed solution was obtained and most of the solvent was removed under vacuum. Adding water into the concentrated green solution and then acetic acid was added drop wise to yield yellow precipitation. The product ([2,2':6',2"-terpyridine]-6,6"-dithiol) was obtained after filtration and washed with water for three times. After dryness, the yellow product ([2,2':6',2"-terpyridine]-6,6"-dithiol) was dissolved in 15 mL 70% nitric acid and heated at 90 ℃ for 2 hours, followed by removing the solvent under vacuum

and then the product 6,6''-disulfonic acid-[2,2':6',2''-terpyridine] (H_2tds) was obtained as light yellow powder (yield: 257 mg, 51%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (d, 2H), 8.45 (d, 2H), 8.18 (t, 1H), 8.04 (t, 2H), 7.83 (d, 2H).

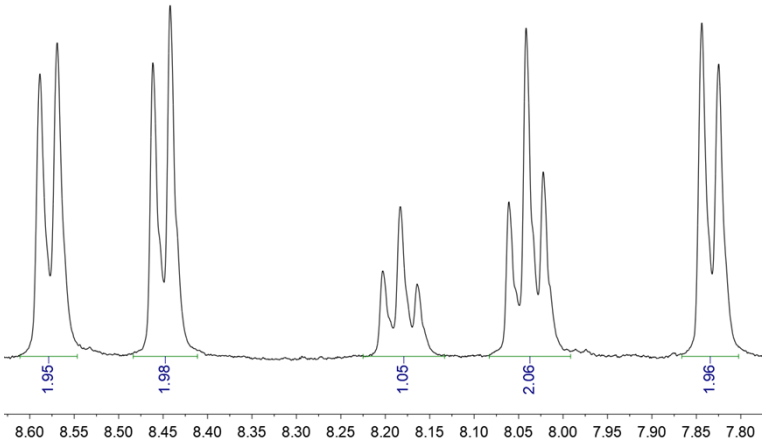

Figure S1. ^{1}H NMR spectrum of H_2tds in DMSO-d_6.

4-(pyrene-1-yl)pyridine (L). A mixture of 1-pyreneboronic acid (246 mg, 1 mmol), 4- bromopyridine hydrochloride (195 mg, 1 mmol), $Pd(OAc)_2$ (23 mg, 0.1 mmol, 10% mol), K_2CO_3 (414 mg, 3 mmol) and tetrabutylammonium bromide (TBAB, 322 mg, 1 mmol), were refluxed under stirring in a mixture of degassed H_2O:toluene (2:9) at 120 °C overnight under argon. After cooling down to r.t., the mixture was filtered and the filtrate was extracted three times with 5 mL of H_2O, the organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed under vacuum. The product was purified by silica column chromatography using a 1:5 mixture of hexane:ethyl acetate to yield ligand L as light yellow powder (167 mg, 60%).^{1}H NMR (400 MHz, Methanol-d_4) δ 8.73 (d, 2H), 8.27 (d, 1H), 8.23 (d, 1H), 8.17 (d, 1H), 8.14 (d, 2H), 8.12 – 8.02 (m, 3H), 7.98 (d, 1H), 7.70 (d, 2H).

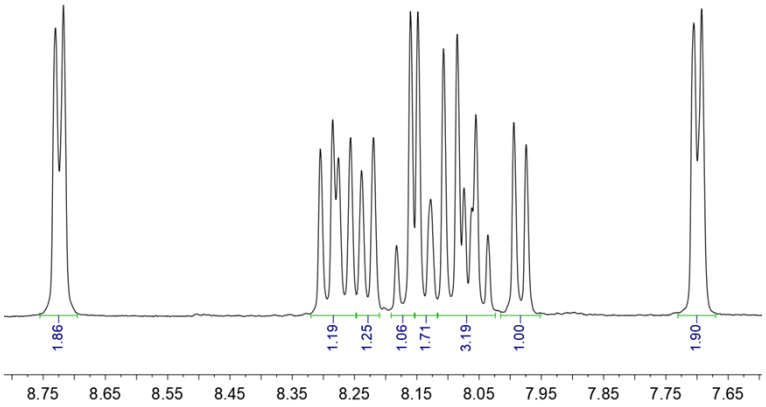

Figure S2. ^{1}H NMR spectrum of L in Methanol-d_4.

Ru(tds)(L)$_2$. To a solution of 6,6"-disulfonic acid-[2,2':6',2"-terpyridine] (79 mg, 0.2 mmol) in dry MeOH (5 mL), dichloro(p-cymene)ruthenium(II) dimer (61 mg, 0.1 mmol), five equivalents of 4-(pyrene-1-yl)pyridine and ten equivalents of Et_3N were added. The resulting mixture was then heated under 125°C for 40 min using a microwave reactor. After cooling to r.t., the mixture was filtered and washed with water, CH_3OH, CH_2Cl_2 and Et_2O, and the product Ru(tds)(L)$_2$ was obtained as dark red powder (yield:137 mg, 65%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (d, 2H), 8.82 (d, 2H), 8.40 (d, 4H), 8.37 – 8.04 (m, 19H), 7.89 (dd, 4H), 7.47 (d, 3H).

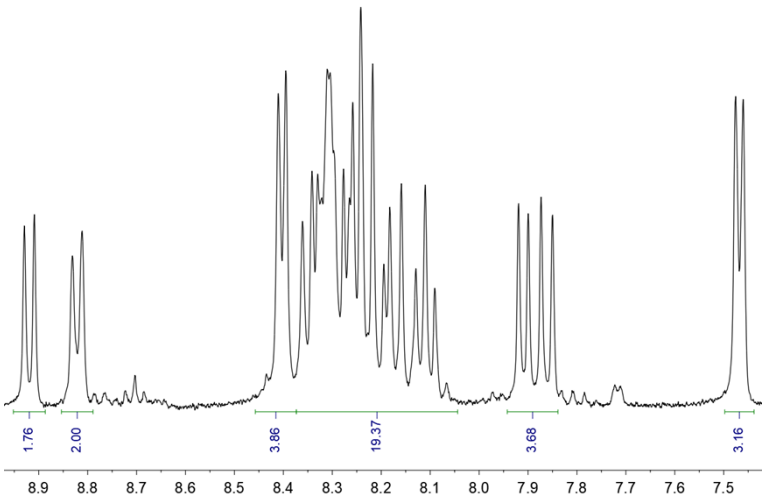

Figure S3. ^{1}H NMR spectrum of **Ru(tds)(L)$_2$** in DMSO-d_6.

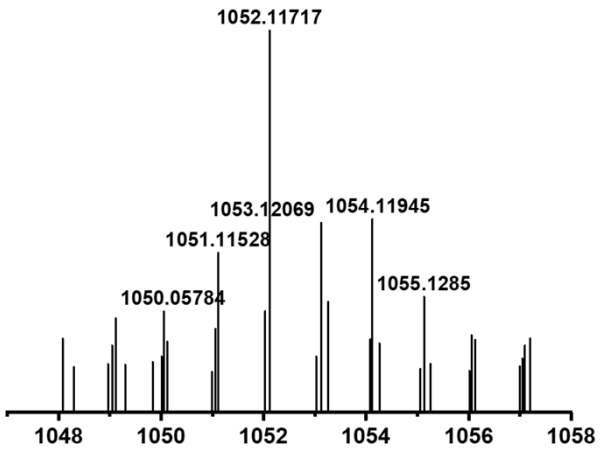

Figure S4. HR-MS of **Ru(tds)(L)$_2$**.

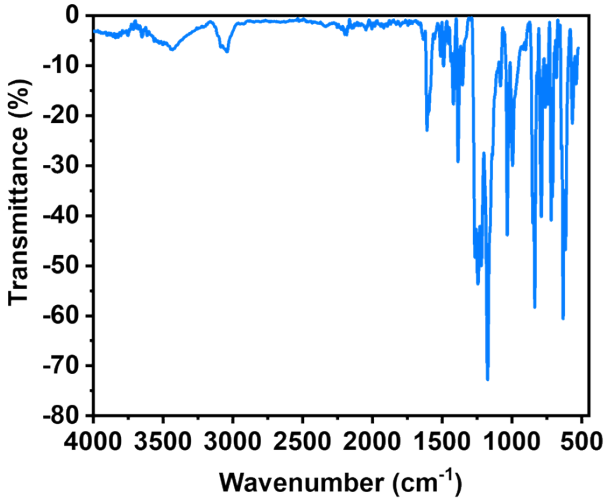

Figure S5. FTIR spectrum of **Ru(tds)(L)$_2$**.

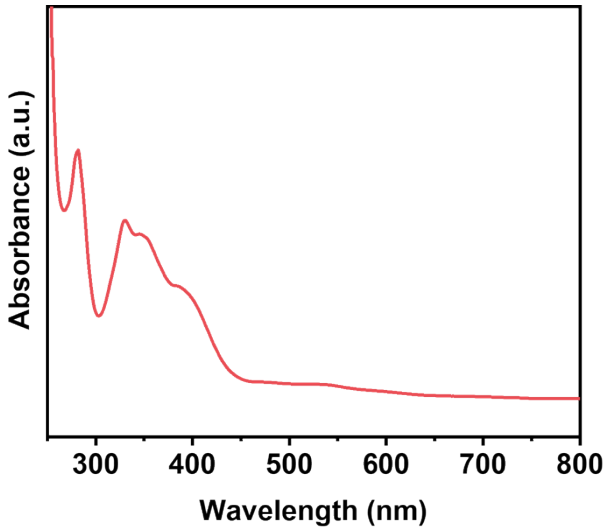

Figure S6. UV-Vis spectrum of **Ru(tds)(L)$_2$**.

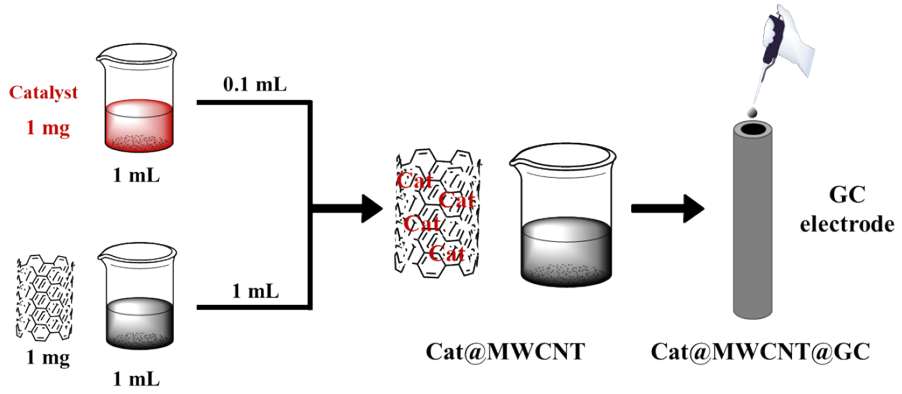

Figure S7. Diagram of preparing the {Ru(tds)$(L)_2$}@MWCNT@GC electrode. The catalyst was adsorbed on the MWCNT by π-π stacking, purified and then anchored on the surface of the GC electrode. For details, see Preparation of {Ru(tds)$(L)_2$}@MWCNT@GC electrode.

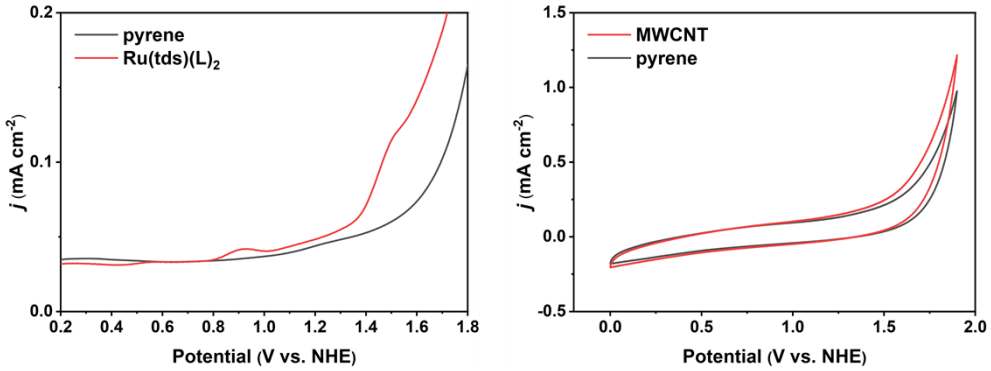

Figure S8. Left, DPV of Ru(tds)$(L)_2$ (0.1 mM, 2.1 mg) and pyrene (0.18 mM, 1 mg) in 0.1 M pH 7 PBS containing 5% trifluoroethanol (TFE). Right, CV of pyrene (0.18 mM, 1 mg) and MWCNT (1 mg) in 0.1 M pH 7 PBS containing 5% TFE, scan rate = 100 mV s^{-1}.

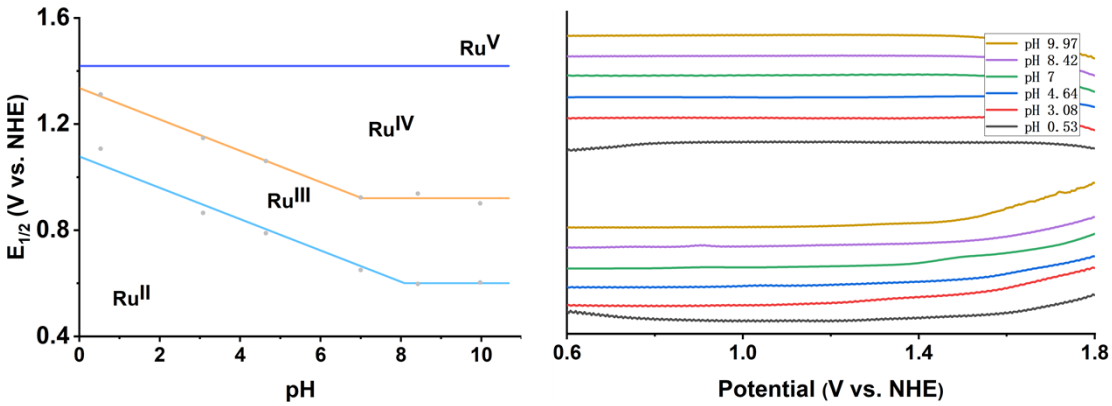

Figure S9. Left, Pourbaix diagram. Right, The differential pulse voltammetry (DPV) of $Ru(tds)(L)_2$ within the pH range (pH 0.53-9.97). Electrolyte preparation: trifluoromethanesulfonic acid solution with pH 0.53, containing 5% trifluoroethanol; PBS with pH 3.08-9.97.

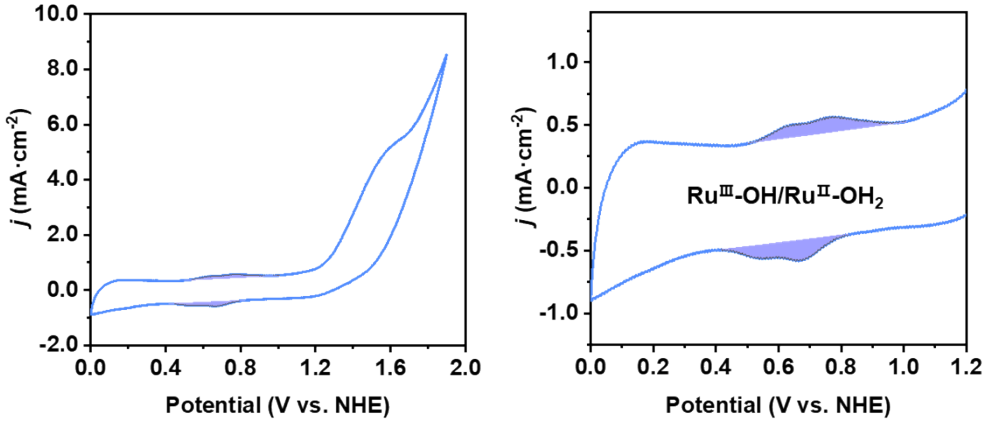

Figure S10. CV of **$Ru(tds)(L)_2$**@MWCNT@GC carried out in a 0.1 M pH 7 PBS at scan rate of 100 mV/s. Purple regions show the area employed for calculating the charge. Cyclic voltammetry shows that the peak separation (ΔEp) is greater than the ideal surface-modified redox couple, indicating that the electrode surface is in a non-uniform electrochemical environment, which is also a common phenomenon where molecular catalysts are non-covalently anchored in mesoporous carbon matrices.

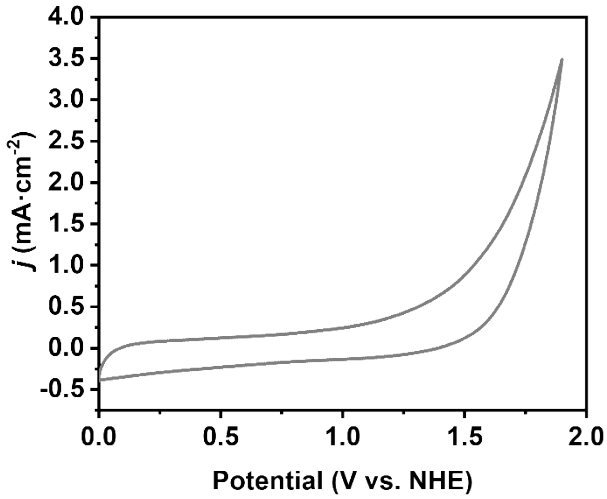

Figure S11. CV of MWCNT@GC carried out in a 0.1 M pH 7 PBS at scan rate of 100 mV/s.

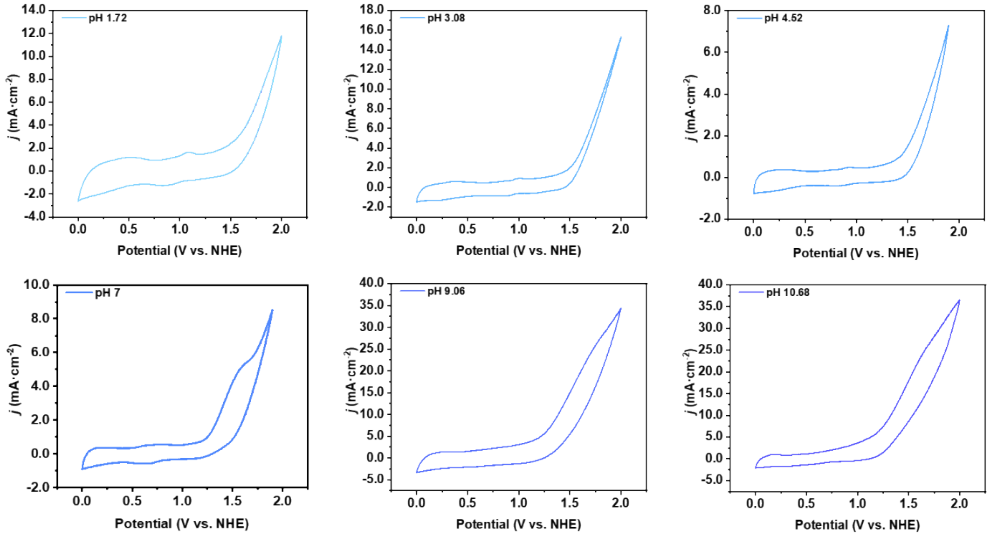

Figure S12. CVs of **Ru(tds)(L)$_2$**@MWCNT@GC under various pH conditions.

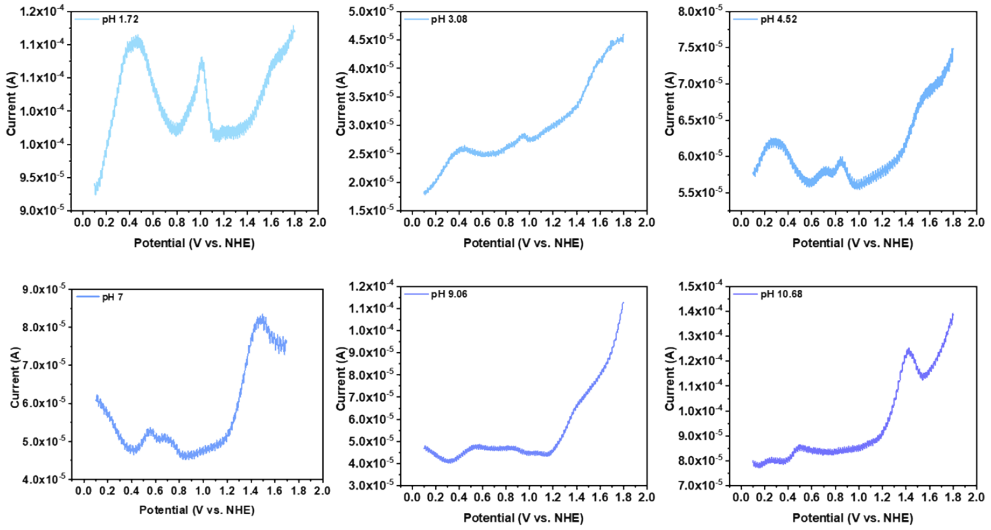

Figure S13. DPVs of **Ru(tds)(L)$_2$**@MWCNT@GC under various pH conditions.

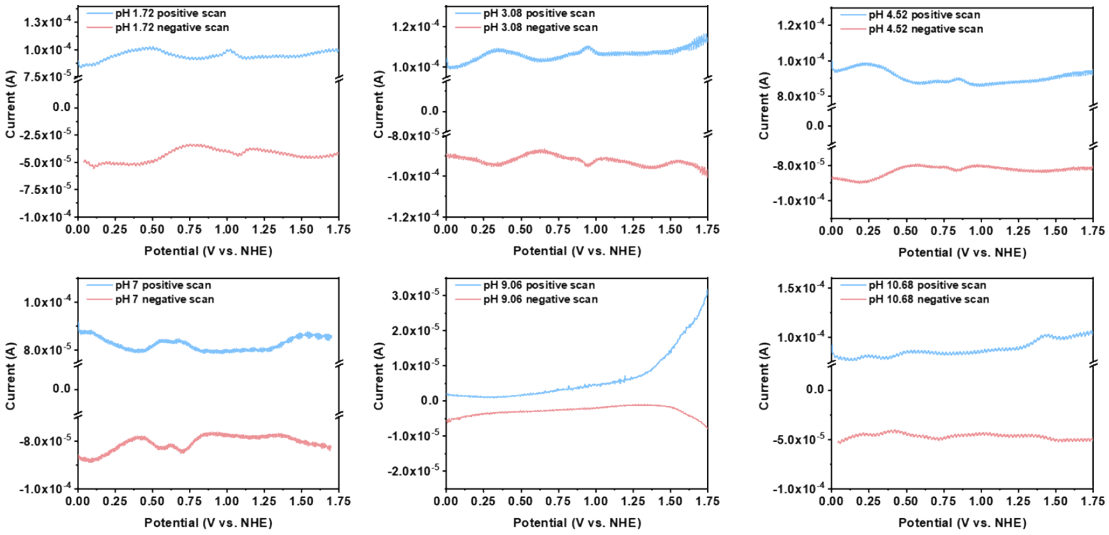

Figure S14. SWVs of **Ru(tds)(L)$_2$**@MWCNT@GC under various pH conditions.

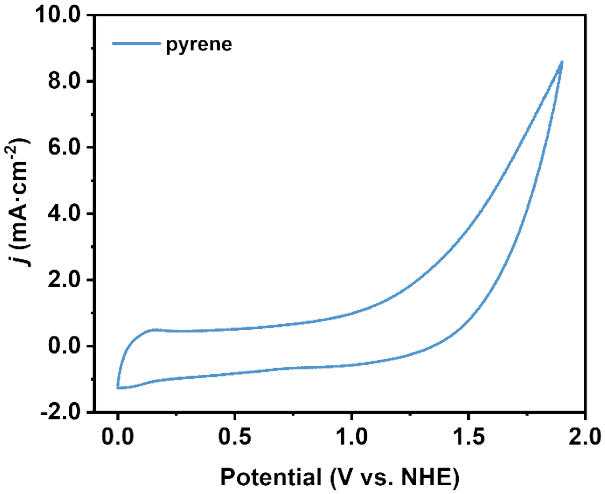

Figure S15. CV of **pyrene**@MWCNT@GC carried out in 0.1 M pH 7 PBS at scan rate of 100 mV/s.

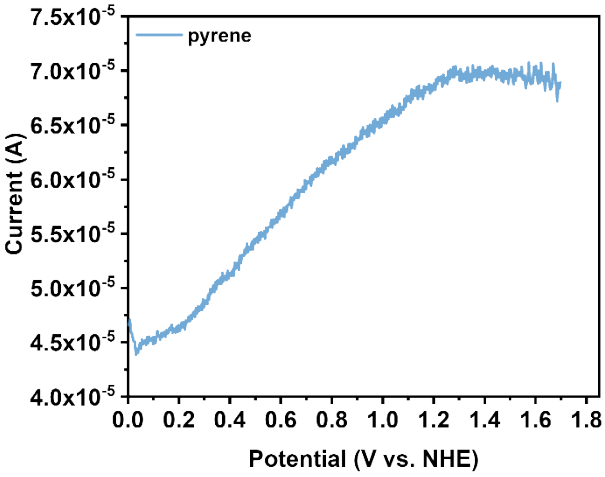

Figure S16. DPV of **pyrene**@MWCNT@GC carried out in 0.1 M pH 7 PBS.

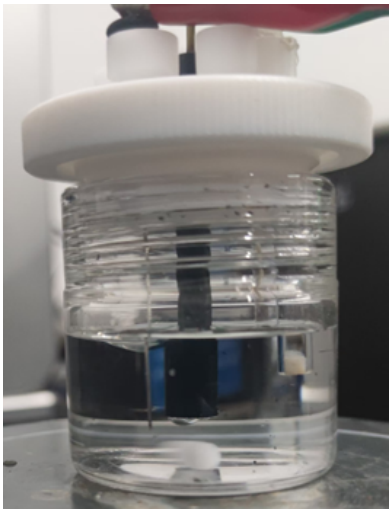

Figure S17. Oxygen bubbles adsorbed on the surface of electrode.

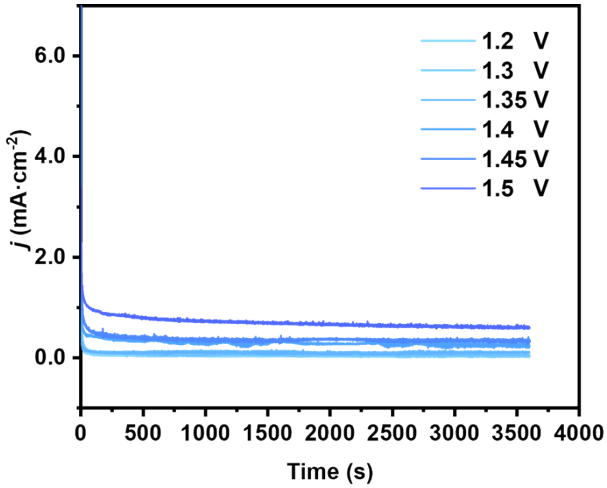

Figure S18. Bulk electrolysis of Ru(tds)$(L)_2$@MWCNT@GC carried out in a 0.1 M pH 7 PBS at different applied potentials.

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