Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Cathodic electrogenerated chemiluminescence of tris(2,2′-bipyridine)ruthenium(II) and peroxydisulfate at pure $Ti_3C_2T_x$ MXene electrodes

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Experimental

Materials and Reagents

We purchased $[Ru(bpy)_3]Cl_2.6H_2O$ from Strem Chemicals (USA), Hexaamineruthenium(III) chloride ($[Ru(NH_3)_6]Cl_3$), benzyl viologen, phosphate buffered saline (PBS) powder (pH 7.4), potassium chloride, lithium perchlorate, lithium fluoride, sodium hydroxide and hydrochloric acid from Sigma-Aldrich (Australia), potassium nitrate, potassium ferricyanide and potassium ferrocyanide from Univar (Australia) and potassium persulfate (potassium peroxydisulfate) from BDH Laboratory Chemicals Division (England). All reagents were used as received. PBS was prepared by dissolving PBS powder in milli-Q, adjusting to the desired pH using HCl or NaOH and further diluting with milli-Q to the desired volume. Solutions of peroxydisulfate and $[Ru(NH_3)_6]^{3+}$ were prepared fresh each day.

MXene synthesis, characterisation and film preparation

The $Ti_3C_2T_x$ MXene was synthesised using an *in situ* HF method.[1, 2] Briefly, 1 g Ti_3AlC_2 MAX phase powder (<40 μm particle size, Carbon-Ukraine) was slowly added to 20 mL of 10 M HCl solution containing 1.6 g lithium fluoride. The etching was carried out for 24 h at 35°C. The resulting dispersion was washed with deionised (DI) water by repeated centrifugation at 3500 rpm (1345 rcf) for 5 min per cycle (Allegra® X-12R Centrifuge, Beckman Coulter) until self-delamination occurred at a supernatant pH ~6. To remove the unreacted MAX phase and multilayer $Ti_3C_2T_x$ MXene, the dispersion was centrifuged at 1500 rpm (247 rcf) for 30 min. The dark green supernatant containing self-delaminated $Ti_3C_2T_x$ MXene sheets was then collected by centrifugation at 7500 rpm (6174 rcf) for 30 min. The resulting dispersion showed a concentration ~45 mg mL^{-1}, which was used to prepare pure $Ti_3C_2T_x$ MXene electrodes. The synthesised $Ti_3C_2T_x$ MXene was characterised using X-ray powder diffraction (XRD, PANalytical X'Pert Powder) using Cu Kα radiation ($\lambda = 1.54$ Å) at a 2θ scan step of 0.013°.

AFM images of $Ti_3C_2T_x$ MXene flakes were obtained using the ScanAsyst scan technology mode of AFM (Bruker, MultiMode 8-HR). The X-ray photoelectron spectroscopy (XPS) data were acquired using a Kratos AXIS Nova equipped with a monochromated Al Kα source ($h\nu$ = 1486.6 eV) operating at 150 W at a step of 0.1 eV. The morphology of the $Ti_3C_2T_x$ MXene film and film thickness were measured using a field emission scanning electron microscope (SEM) (Zeiss SUPRA 55-VP). $Ti_3C_2T_x$ MXene electrode samples were prepared by brittle fracture in liquid nitrogen and $Ti_3C_2T_x$ MXene films would break and separate from the polymer substrate to enable us to study the $Ti_3C_2T_x$ MXene film thickness.

The $Ti_3C_2T_x$ MXene electrodes were prepared based on commercial 4 mm screen-printed electrodes (SPEs, GSI Technologies). First, the carbon working electrode was removed using a sharp blade. Then the electrode was masked by removable tape (Scotch® 811, thickness of ~40 µm) with 5 mm diameter circular holes. The holes were placed in the same position as the removed carbon electrodes. Afterwards, the synthesised $Ti_3C_2T_x$ MXene dispersion was coated on the masked electrodes using blade coating method and the mask was removed after the $Ti_3C_2T_x$ MXene dispersion was dried at room temperature for 6 h in an argon atmosphere. The thickness of $Ti_3C_2T_x$ MXene electrode was ~450 nm, which was measured from the SEM image of the film cross-section. The $Ti_3C_2T_x$ MXene electrode showed high conductivity of 8100 S cm^{-1} (measured using Ossila four-point probe system).

Electrochemistry and ECL

All $Ti_3C_2T_x$ MXene electrodes were stored under grade 5 argon in a sealed container prior to analysis to avoid the surface degradation of $Ti_3C_2T_x$ MXene electrodes in air. We conducted electrochemical and ECL measurements in a custom-built Faraday cage using an Autolab PSTAT 204 or Autolab 128N potentiostat and an ET Enterprises model 9828B extended-range trialkali S20 photomultiplier tube (PMT). The electrode was housed in a custom-made 3D printed cell and interfaced with the potentiostat using a Dropsens cable connector and each electrode was used once. All potentials are recorded versus the Ag/AgCl pellet reference electrode. We calculated ECL intensities by applying a 5 or 10 s chronoamperometric pulse to -2.25 V (see Figure S7) and integrating the area using NOVA software. To obtain photographs of the ECL at $Ti_3C_2T_x$ MXene film electrodes, we used a Canon 6D camera (Canon Inc, Japan) equipped with a 100 mm F2.8 macro lens (Tamron Inc, Japan) and applied a 100 s chronoamperometric pulse to -2.5 V. Exposure: F2.8, ISO 3200, 100 s.

Supplementary Figures

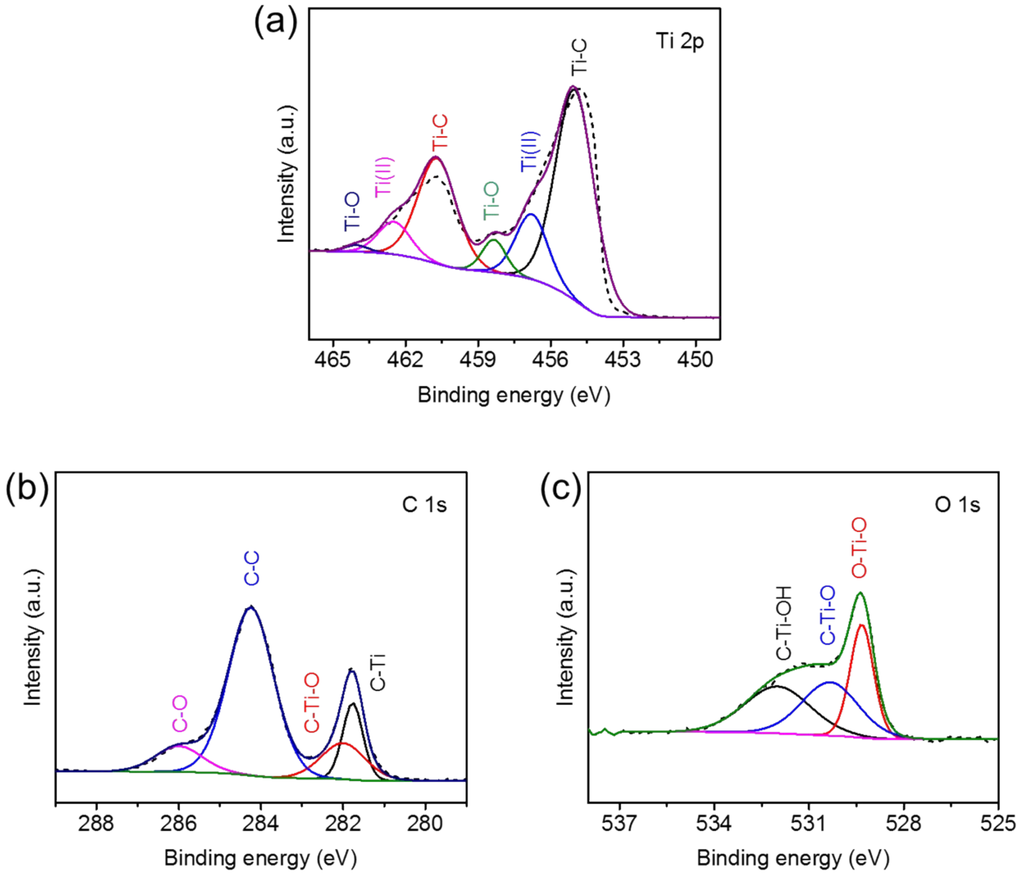

Figure S1. High-resolution XPS spectra of (a) Ti 2p, (b) C 1s and (c) O 1s from the $Ti_3C_2T_x$ MXene electrode.

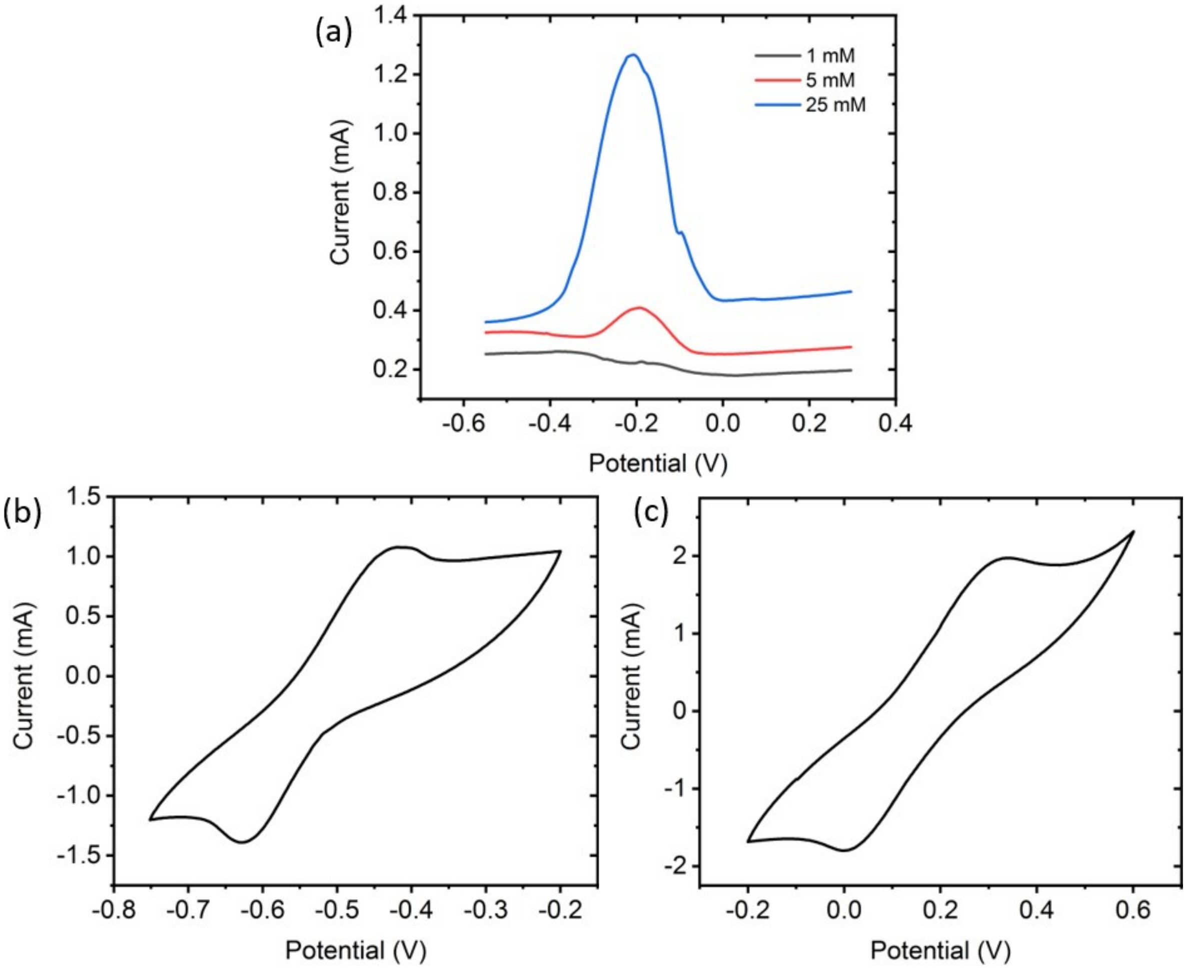

Figure S2. (a) Square wave voltammetry of $[Ru(NH_3)_6]^{3+}$ at the $Ti_3C_2T_x$ MXene film electrode, 0.1 M KCl electrolyte degassed with grade 5 argon, step potential 5 mV, amplitude 20 mV, frequency 25 Hz. Cyclic voltammetry of (b) benzyl viologen (25 mM) and (c) $[Fe(CN)_6]^{3-/4-}$ (25 mM equimolar solution) at $Ti_3C_2T_x$ MXene electrode, 0.1 M KCl degassed with grade 5 argon, scan rate 0.1 V s^{-1}.

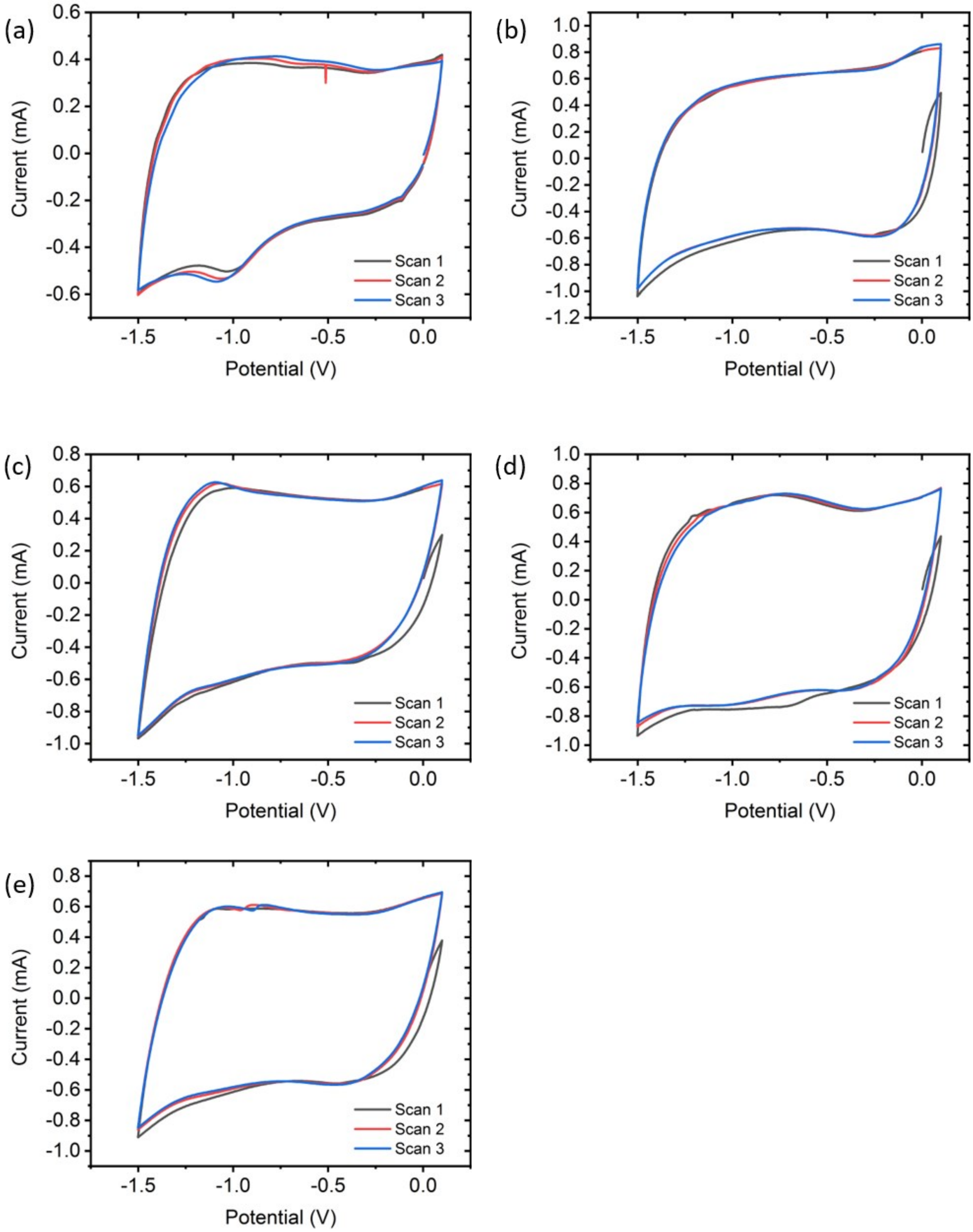

Figure S3. (a) Cathodic cyclic voltammogram of the $Ti_3C_2T_x$ MXene film electrode, PBS, pH 7.4, (b) grade 5 argon degassed PBS, pH 7.4 (c) grade 5 argon degassed 0.1 M KCl, (d) grade 5 argon degassed 0.1 M $LiClO_4$, (e) grade 5 argon degassed 0.1 M KNO_3. Scan rate 0.1 V s^{-1}.

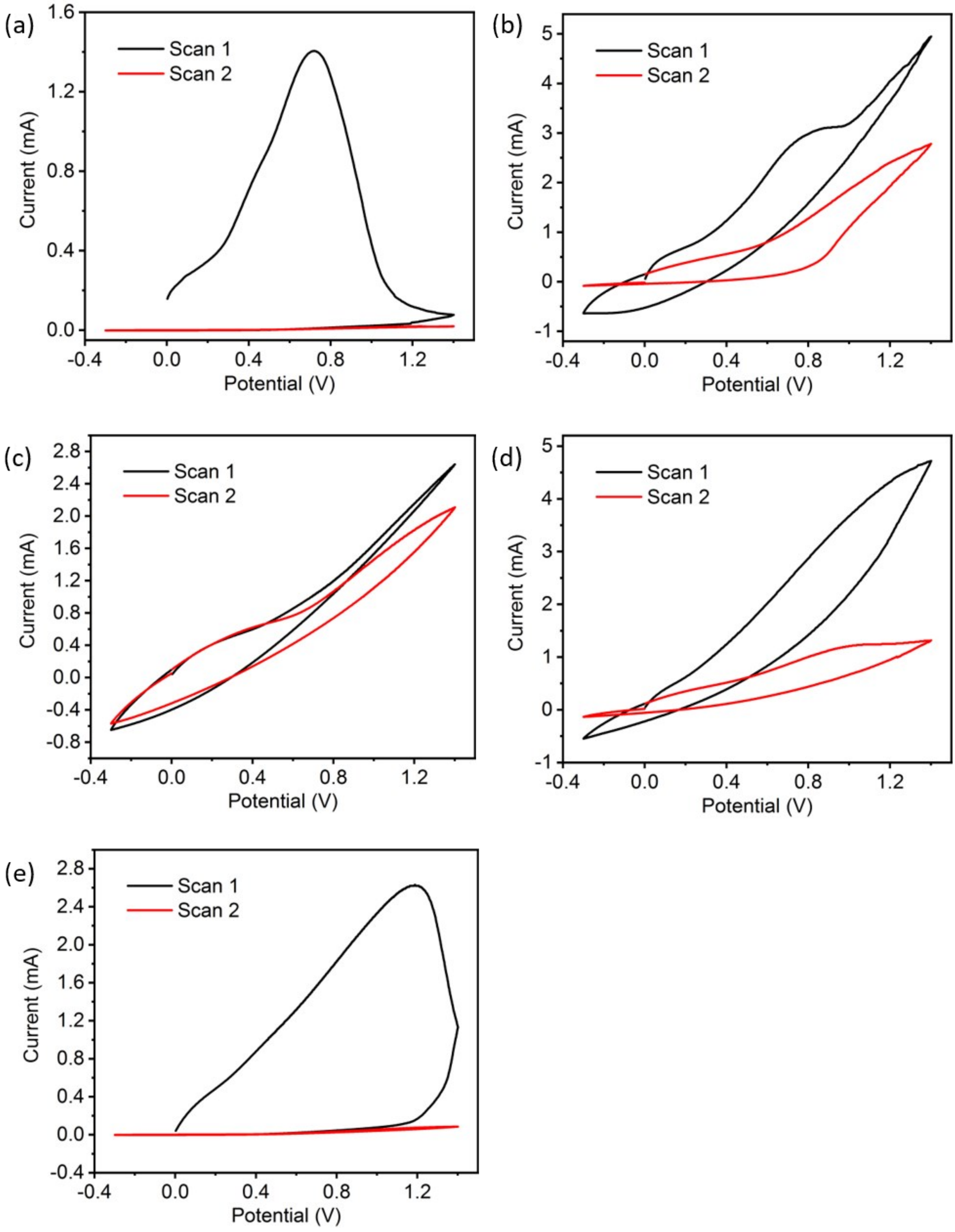

Figure S4. (a) Anodic cyclic voltammogram of the $Ti_3C_2T_x$ MXene film electrode, PBS, pH 7.4, (b) grade 5 argon degassed PBS, pH 7.4 (c) grade 5 argon degassed 0.1 M KCl, (d) grade 5 argon degassed 0.1 M $LiClO_4$, (e) grade 5 argon degassed 0.1 M KNO_3. Scan rate 0.1 V s^{-1}.

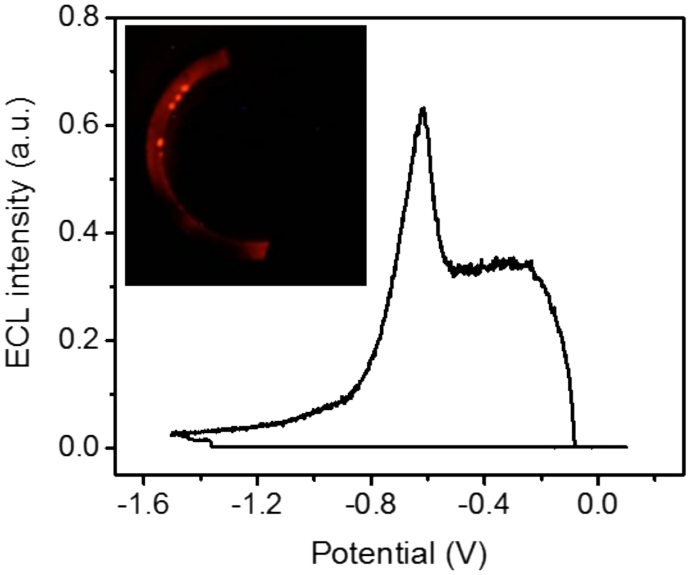

Figure S5. Counter electrode ECL of TPA with 10 µM $[Ru(bpy)_3]^{2+}$. PMT response in cathodic cyclic voltammogram scan range, 100 mM TPA in 0.1 M PBS, pH 7.4. Figure inset represents a photograph of the $Ti_3C_2T_x$ MXene film electrodes, 100 s chronoamperometric pulse to -0.8 V.

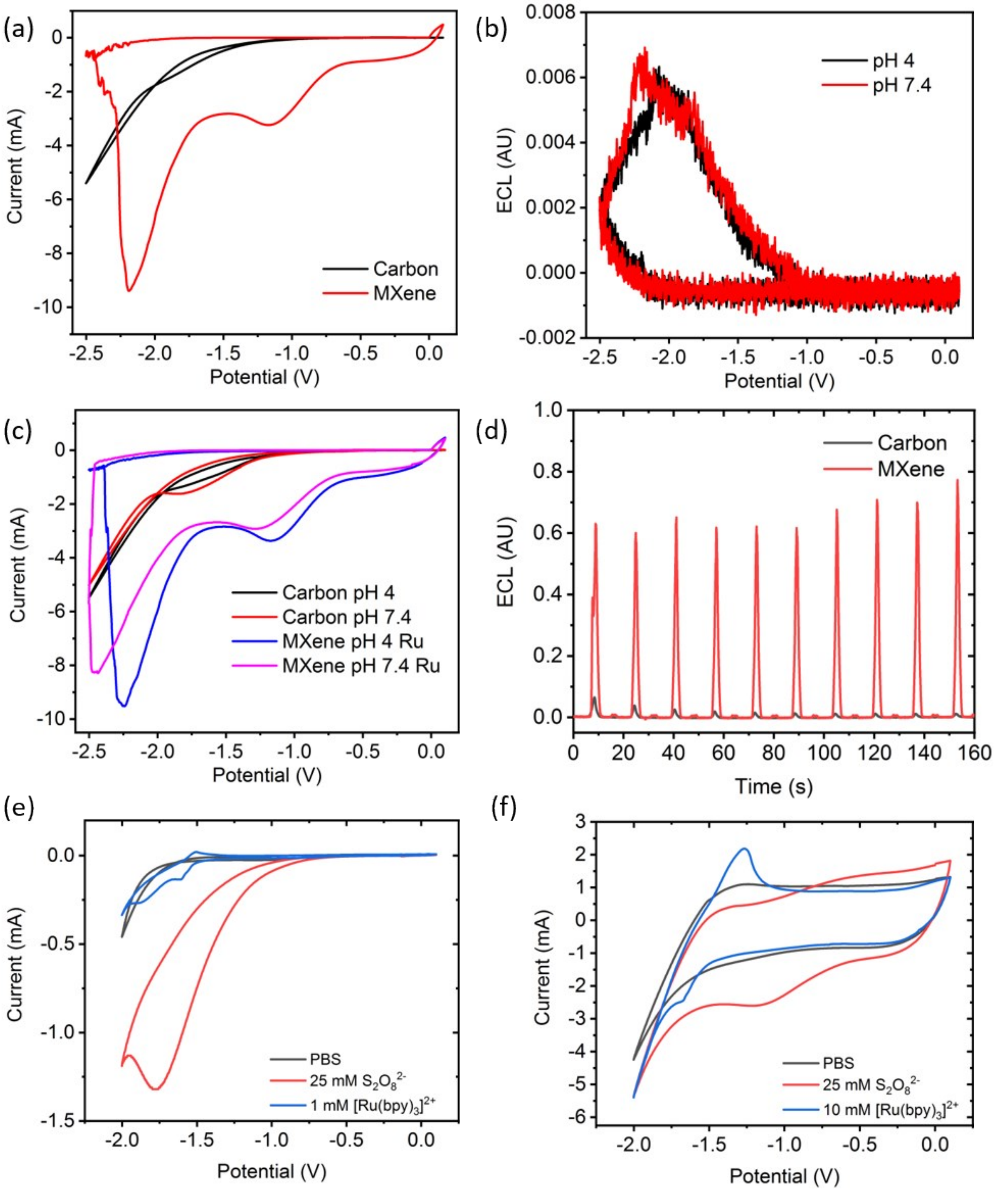

Figure S6. (a) Current recorded from cathodic cyclic voltammogram scan of carbon and $Ti_3C_2T_x$ MXene film electrodes, 25 mM $S_2O_8^{2-}$, in PBS, 0.25 V s^{-1}. (b) Blank ECL intensity of 5 mm $Ti_3C_2T_x$ MXene film electrodes, 25 mM $S_2O_8^{2-}$, in PBS, 0.25 V s^{-1}. (c) Current response curves for Figure 2b, 5 μM $[Ru(bpy)_3]^{2+}$ and 25 mM $S_2O_8^{2-}$ in PBS using 5 mm diameter $Ti_3C_2T_x$ MXene film working electrode and 5 mm diameter working electrode carbon SPEs, and a scan rate of 0.25 V s^{-1}. (d) Stability of the ECL signal over successive cyclic voltammetry scans, 5 µM $[Ru(bpy)_3]^{2+}$ and 25 mM $S_2O_8^{2-}$ in PBS using 5 mm diameter $Ti_3C_2T_x$ MXene film and 5 mm diameter carbon SPEs, 0.25 V s^{-1}. Current response of (e) GSI 5 mm diameter carbon SPEs and (f) 5 mm diameter $Ti_3C_2T_x$ MXene film in PBS buffer (black line), 25 mM $S_2O_8^{2-}$ in PBS (red line) and $[Ru(bpy)_3]^{2+}$ (10 mM concentration at $Ti_3C_2T_x$ MXene film and 1 mM at carbon SPE) in PBS (blue line).

Table S1: Reproducibility of ECL signal at 5 mm diameter $Ti_3C_2T_x$ MXene film and 5 mm diameter carbon SPEs. Results determined from three replicate measurements of the ECL peak height from four successive CV scans on three separate electrodes (for each scan n = 3 separate electrodes). "All" represents the average and standard deviation determined from all four scans at all three electrodes (n = 12).

	$Ti_3C_2T_x$ MXene film		Carbon SPEs	
	Average	RSD	Average	RSD
Scan 1	0.53	16%	0.07	3%
Scan 2	0.63	12%	0.04	2%
Scan 3	0.64	12%	0.03	2%
Scan 4	0.62	18%	0.02	6%
All	0.61	15%	0.04	45%

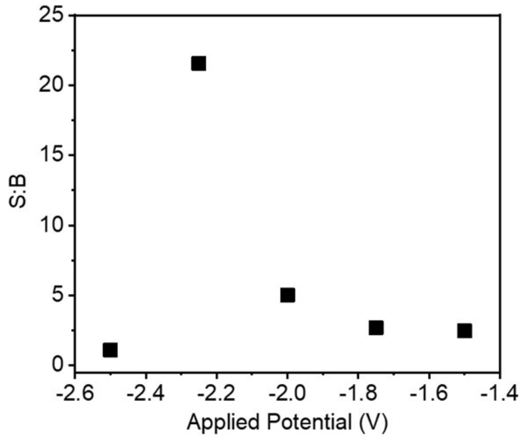

Figure S7. Optimal potential determination, S:B is the ratio of the ECL signal from solutions with 1 µM $[Ru(bpy)_3]^{2+}$ to ECL signal from solutions without $[Ru(bpy)_3]^{2+}$. Conditions: 10 mM $S_2O_8^{2-}$, 1 µM $[Ru(bpy)_3]^{2+}$ in PBS pH 7.4; 10 s applied chronoamperometric pulse to designated potential; blank tested in singlicate; sample response calculated as the average of three replicate determinations on three separate electrodes.

References

1. J. Zhang, S. Seyedin, S. Qin, Z. Wang, S. Moradi, F. Yang, P. A. Lynch, W. Yang, J. Liu, X. Wang and J. M. Razal, *Small*, 2019, **15**, 1804732.
2. M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin and Y. Gogotsi, *Chem. Mater.*, 2017, **29**, 7633-7644.