

# Heterogenization of Molecular Chalcogenides for Electro- & Photochemical H<sub>2</sub> Production

## Supplementary information

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## Supplementary information

### Experimental section

General experimental: All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. SWCNT-CO<sub>2</sub>H were obtained from Ossila and used as received. FT-IR spectra were recorded on a Nicolet summit lite Everest ATR-FT-IR and collected in transmission mode.

### Experimental

**(NMe<sub>4</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>S<sub>8</sub>] (1):** Prepared according to the literature procedures.<sup>1</sup> S<sub>8</sub> (8g) is suspended in 100mL 20% NH<sub>4</sub>OH. H<sub>2</sub>S is bubbled through the suspension with stirring, until no more elemental Sulfur is present, giving a deep red polysulfide solution. Separately, (NH<sub>4</sub>)<sub>4</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (21g, 17 mmol) is dissolved in 20% NH<sub>4</sub>OH and heated to 90°C. Upon complete dissolution, the polysulfide solution is added to the Mo solution and the reaction mixture is heated to 90-95°C for 90 minutes. The solution is then allowed to cool to room temperature, and NMe<sub>4</sub>Cl (10g, excess) is added to precipitate the final product, which is then filtered under vacuum and washed with cold EtOH, Et<sub>2</sub>O and CS<sub>2</sub>. The product is used in the next step without further purification.

**(NMe<sub>4</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>Se<sub>6</sub>] (2):** Prepared according to the literature procedures.<sup>2</sup> Elemental selenium (2.37 g, 30 mmol) is suspended in 5% aqueous ammonia solution (100 mL) and degassed by bubbling through nitrogen. The exhaust gas is passed through a bleach trap to capture and deactivate any hydrogen selenide produced. Sodium borohydride (236 mg, 6.25 mmol) in water (10 mL), degassed by bubbling through nitrogen and added slowly to reduce the selenium, producing a dark red solution which is heated to 50°C for 40 minutes with stirring under a nitrogen atmosphere. This solution is then added to a degassed solution of (NH<sub>4</sub>)<sub>4</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (1.77 g, 1.4 mmol Mo<sup>VI</sup>) in water (50 mL) and stirred overnight under a flow of nitrogen. NMe<sub>4</sub>Cl (10 g, excess) is dissolved in a minimum amount of water and added to the solution to precipitate a dark brown solid (NMe<sub>4</sub>)<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>Se<sub>6</sub>] which is collected by vacuum filtration and washed with cold water, cold ethanol, diethyl ether and carbon disulfide. The product is used in the next step without further purification.

## Synthesis of composite materials

To 3 mL acetone was added  $(\text{NMe}_4)_2[\text{Mo}_2\text{O}_2\text{S}_8]$  (280 mg, 0.45 mmol), with stirring until the solution became saturated at which point it was then syringe filtered (Nylon, 0.22  $\mu\text{m}$ ) to obtain a clear dark red solution of  $(\text{NMe}_4)_2[\text{Mo}_2\text{O}_2\text{S}_8]$ . SWCNT-CO<sub>2</sub>H (5mg) was then added to the solution and stirred for 3 days. The suspension was then filtered under vacuum and washed with acetone.

An analogous procedure was used to for  $(\text{NMe}_4)_2[\text{Mo}_2\text{O}_2\text{Se}_6]$ , with the following adjustments: The Mo species (238 mg, 0.28 mmol) was dissolved in DMF (3mL). Upon filtering the dimer solution onto the SWCNTs, the solution was degassed with N<sub>2</sub> for 5 minutes, then sealed with a septum. A N<sub>2</sub> balloon was attached, and the solution was left stirring as above.

## Electrochemistry

### Electrochemical measurements:

Electrochemical measurements were made using a CH Instruments CHI600D potentiostat in a custom made three electrode electrochemical cell. 1M H<sub>2</sub>SO<sub>4</sub> (pH ~0) was used as the electrolyte. The working electrode was a glassy carbon electrode (GCE) (BASi, d = 3.0 mm, A = 0.071 cm<sup>2</sup>) onto which the catalyst under investigation had been deposited as described in the electrode preparation section. A graphite rod served as the counter electrode and an Ag/AgCl as reference electrode (3 M KCl, BASi). The electrolyte and headspace were thoroughly degassed with N<sub>2</sub> or Ar gas for 10 minutes before the measurement. The electrode potentials can be converted to NHE according to the equation  $E(\text{NHE}) = E(\text{Ag}/\text{AgCl}) + 0.21 \text{ V}$ . The polarisation curves are measured by LSV with a scan rate of 5 mV s<sup>-1</sup>. All measurements recorded have been iR corrected to compensate for electrolyte resistance.

### Electrode preparation

Working electrodes were prepared by drop casting and drying a catalytic ink containing the respective Mo composite species on the surface of a glassy carbon electrode. Before applying the ink, the surface of the electrode was polished to a mirror finish with an aqueous slurry of 0.05  $\mu\text{m}$  alumina powder on a nylon polishing pad (Alvatek), followed by washing with deionised water. The electrode was then cleaned

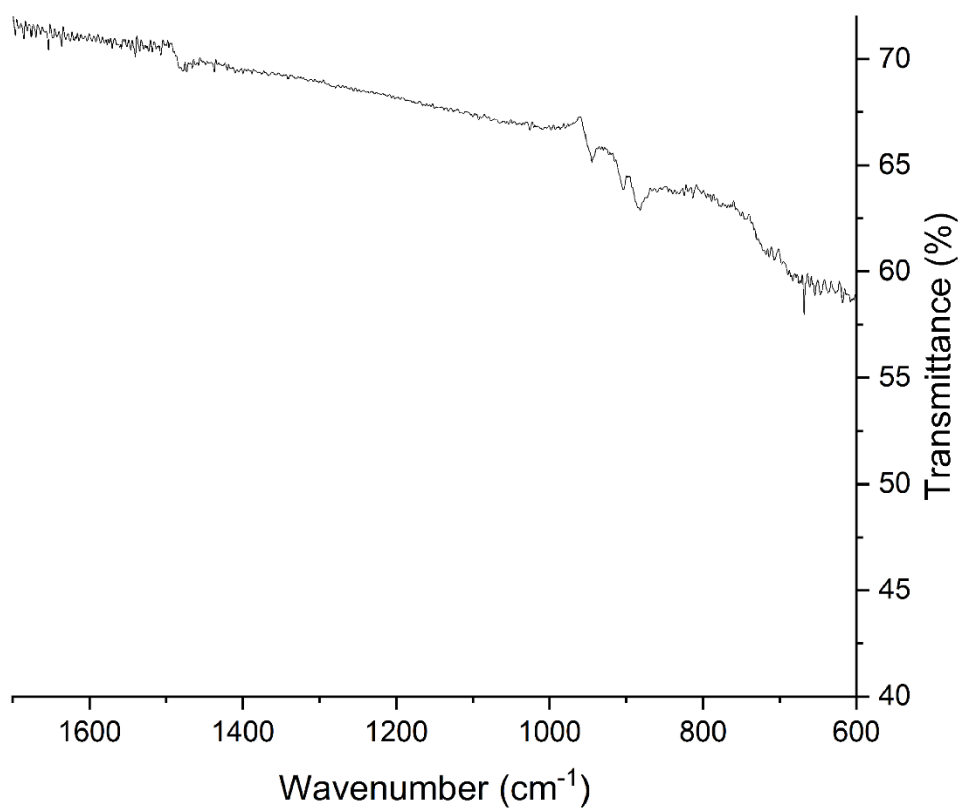
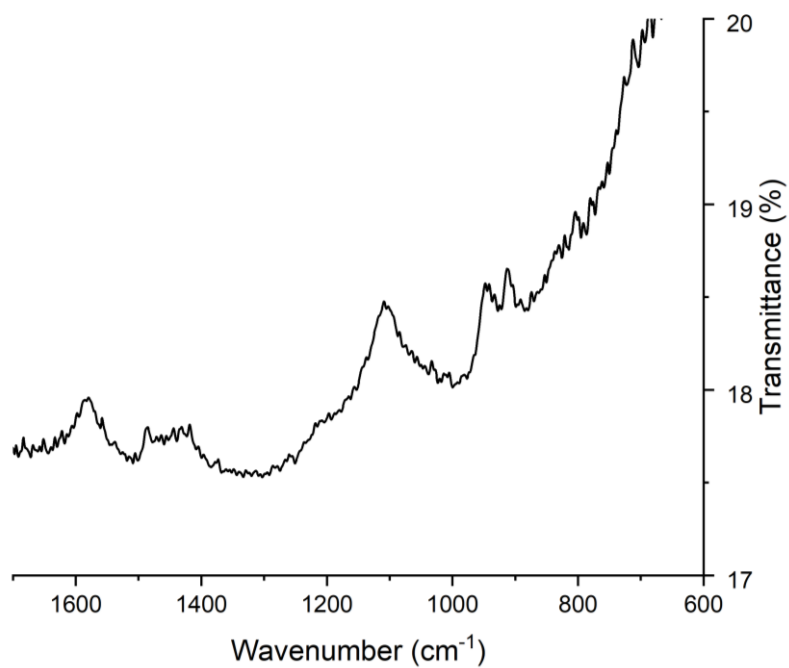
electrochemically by cyclic voltammetry at 1 to  $-1.2$  V for 50 cycles at a scan rate of  $100 \text{ mV s}^{-1}$ . Catalytic inks were prepared in acetone. The inks consisted of  $\{\text{Mo}_2\}@\text{SWNCT-CO}_2\text{H}$  (5 mg) in Acetone (250  $\mu\text{L}$ ) and 5% Nafion solution (50  $\mu\text{L}$ ). The inks were sonicated to give a homogenous mixture. 5  $\mu\text{L}$  portions were drop-casted on the GC electrode surface and dried at room temperature. In the case of the reference measurements, stock solutions of the dimers were prepared in acetone such that 250  $\mu\text{L}$  contained the same catalytic loading. These were then added to 4.2 mg Carbon powder and 50  $\mu\text{L}$  Nafion solution as stated previously.

## Photochemistry

**Photochemical measurements:** Photochemical measurements were carried out in a 20 mL borosilicate glass tube, sealed with a rubber septum. All measurements were conducted in aqueous media (10 mL, adjusted to pH 7 using concentrated  $\text{HCl}_{(\text{aq})}$ ), with triethanolamine (TEOA, 15% v/v) as a sacrificial electron donor and Eosin Y (EY, 0.4 mM) as a photosensitiser. In both instances, 7 mg of heterogenized material was used as the active catalyst, and the reaction mixture was irradiated under constant stirring. The reaction mixture was degassed with Ar for 5 minutes to remove dissolved oxygen from the solution. Samples were analysed by GC at regular intervals (approx. 30 minutes). The light source used was a 100W ozone free Xe lamp (Newport), and the sample was kept 50 cm from the source.

## Electrochemical stability measurements

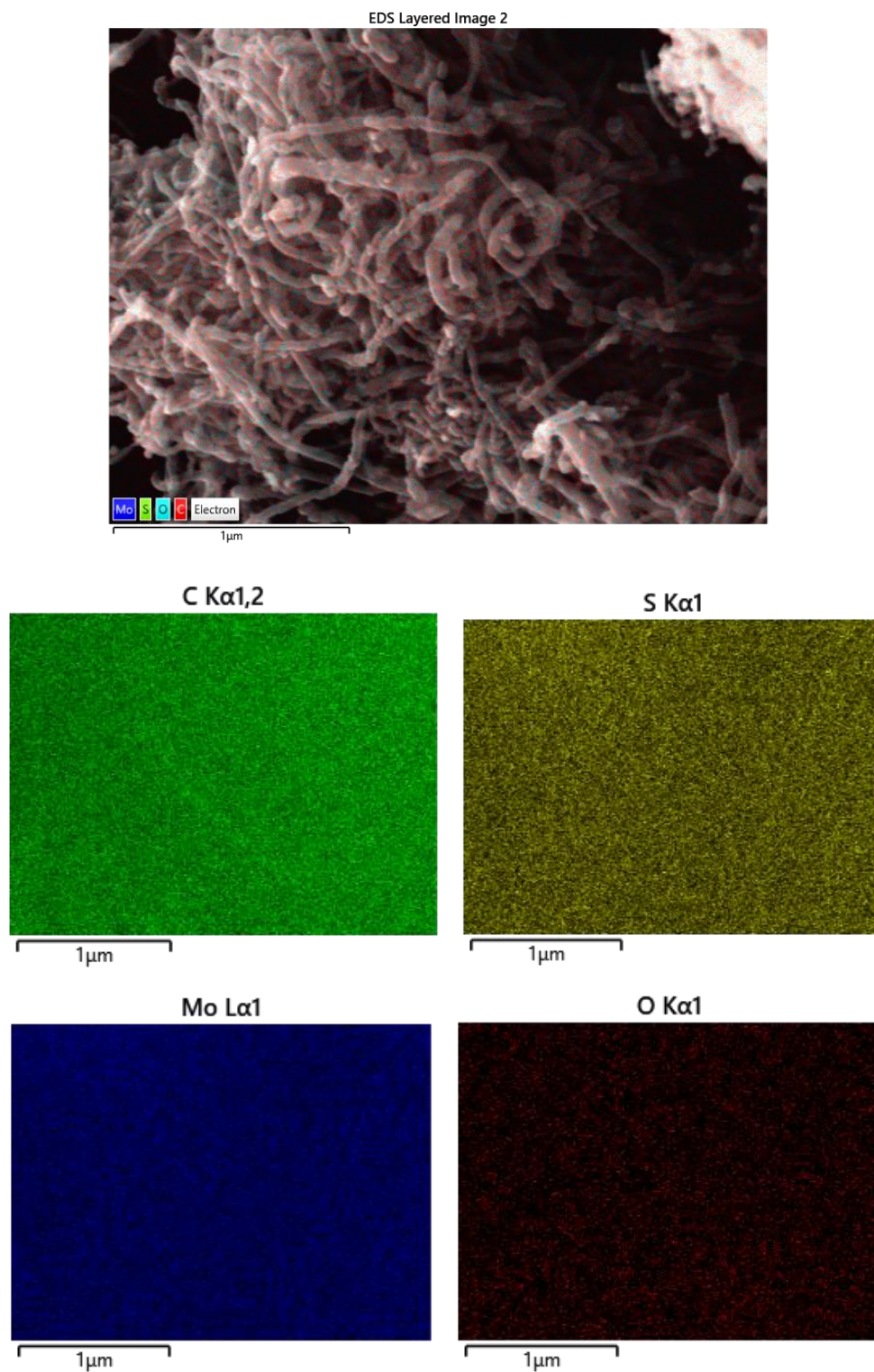
In order to verify the long-term stability of the catalytic materials, cyclic voltammetry was employed at a scan rate of  $100 \text{ mVs}^{-1}$  for 1000 cycles between 0 and  $-390 \text{ mV}$  (vs Ag/AgCl) as a modest approximation of start-up/shut down of an electrolyser in acidic conditions as described above, recording LSVs at 0, 500 and 1000 cycles. Cyclic voltammetry in organic media (0.5 M  ${}^n\text{Bu}_4\text{NPF}_6$  (TBAPF<sub>6</sub>) in dry, degassed MeCN, 25 mL) was performed before and after this cycling process to ensure the chemical stability of the catalytic composites. Catalytic inks drop casted on GCE according to the procedure described above (**Fig S8-S9**).



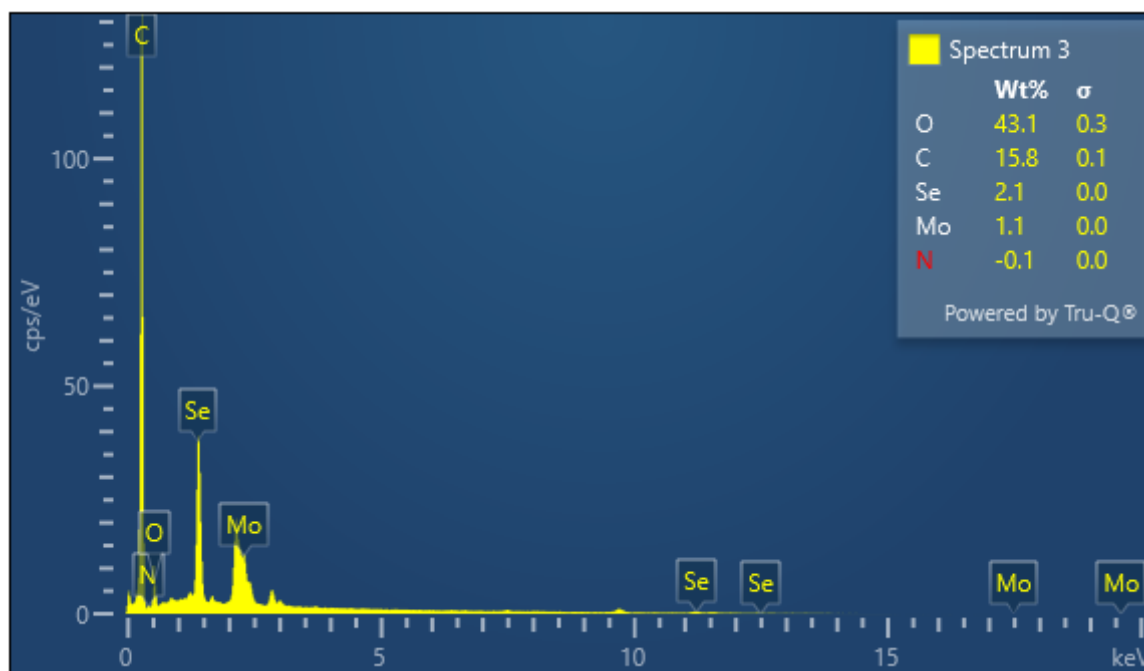
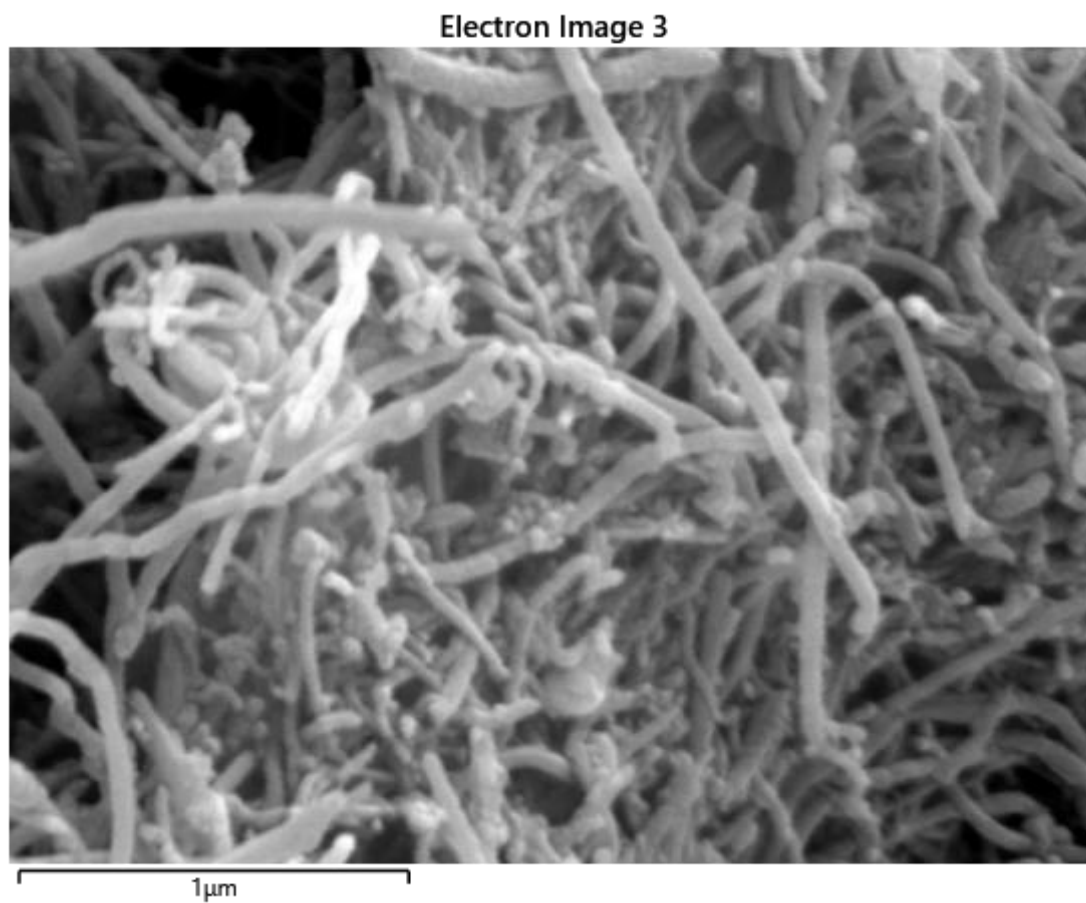
**Figure S1:** FT-IR ATR spectrum of **1@SWCNT** (top) and **2@SWCNT** (bottom). Characteristic Mo=O stretching frequency centred around 900-950 cm<sup>-1</sup>.

## SEM/EDS

SEM measurements were carried using a TESCAN CLARA ultra high resolution scanning electron microscope (UHR-SEM). All samples were sputter coated with Au prior to measurement. EDS measurements were carried out on an Oxford Instruments Ultim Max 65.



**Figure S2:** EDS layered SEM image of material 1@SWCNT (top), elemental distribution shown below.

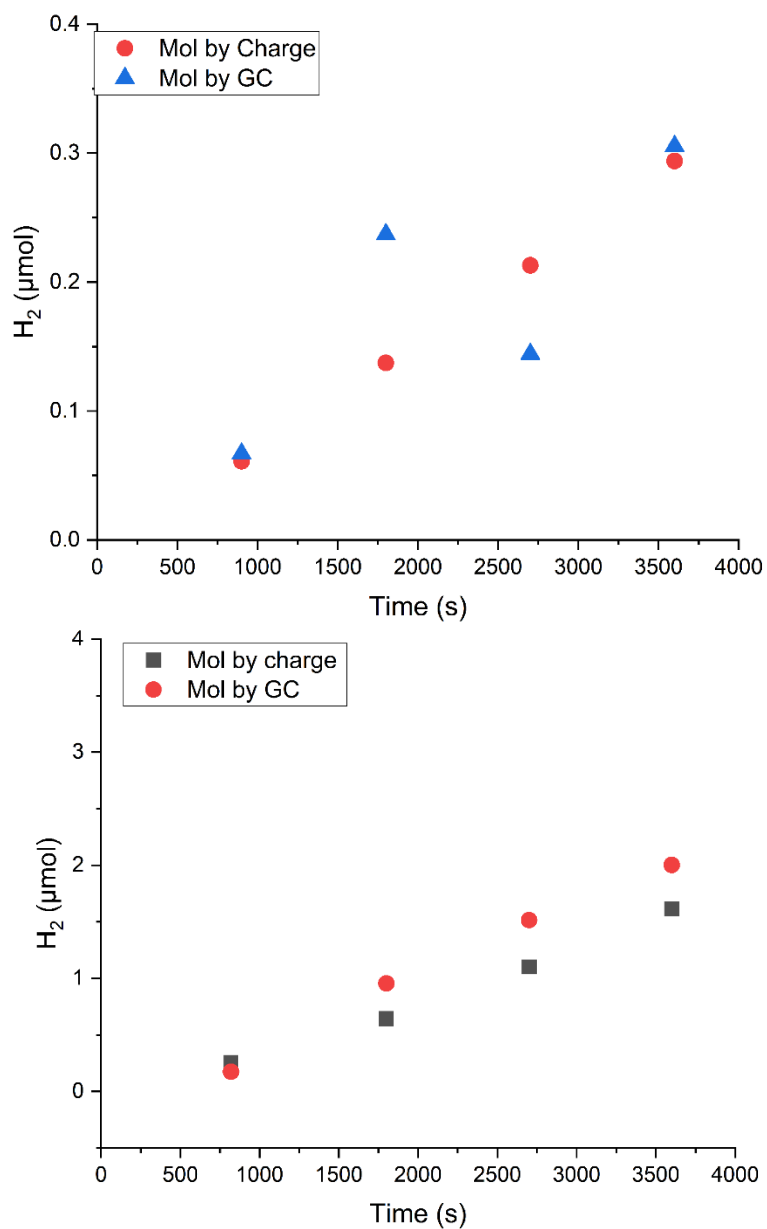


**Figure S3:** EDS measurement of material 2@SWCNT, with SEM image of analysed region above.

## Gas Chromatography

Gas chromatography measurements were conducted utilizing an Agilent 8860 gas chromatograph system outfitted with a thermal conductivity detector (TCD). This system was configured with two Porapak Q columns and a MoleSieve 13X column. The initial oven temperature is set to 50°C and held for 4 minutes, followed by a temperature ramp of 10°C per minute until reaching 120°C. The total analysis time is 11 minutes. Prior to the analysis, the GC system was calibrated using certified hydrogen gas standards (5%, 3%, 2%, and 1% H<sub>2</sub>) sourced from CK Gas Product Limited, U.K. Faradaic efficiency measurements were conducted using the same preparation method described as above. A constant potential of 500 mV (vs RHE) (**1@SWCNT**) and 390 mV (vs RHE) for (**2@SWCNT**) respectively, and 250 µL samples of the headspace gas were injected into the GC at 15-minute intervals. The faradaic efficiency was calculated using the Faraday equation,  $N(\text{H}_2) = Q/nF$ , that is the number of moles of H<sub>2</sub>,  $N(\text{H}_2)$ , is equal to the charge passed divided by the number of reacting electrons (2) multiplied by faraday's constant. This is then plotted against the calculated moles of H<sub>2</sub> in the headspace as measured by gas chromatography.

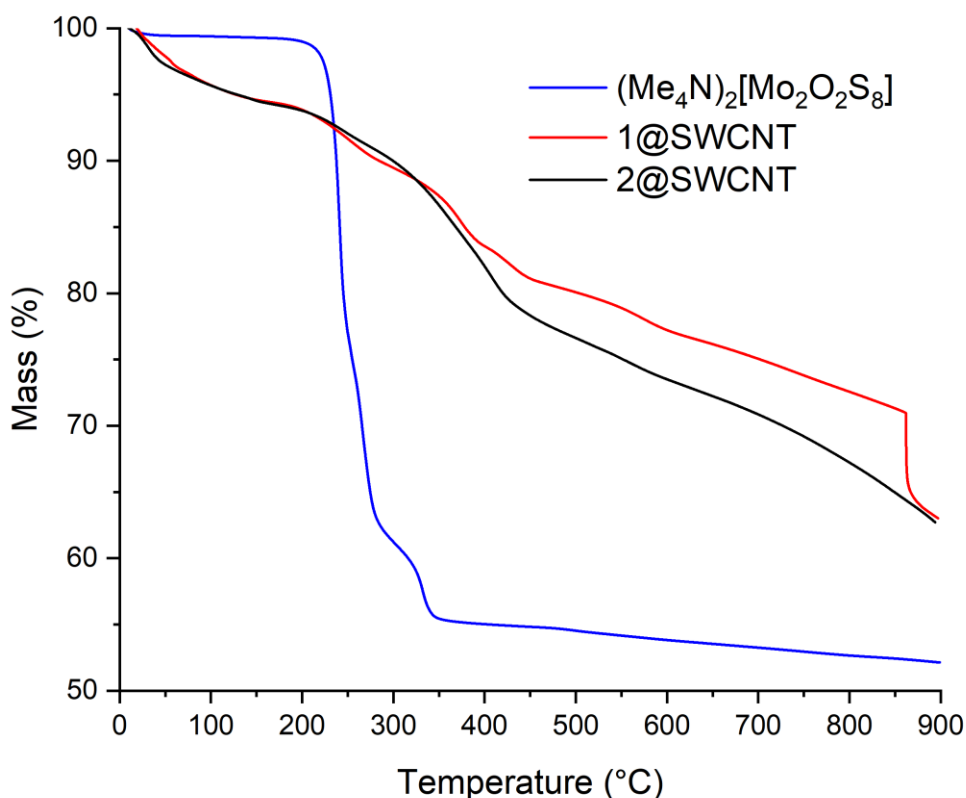




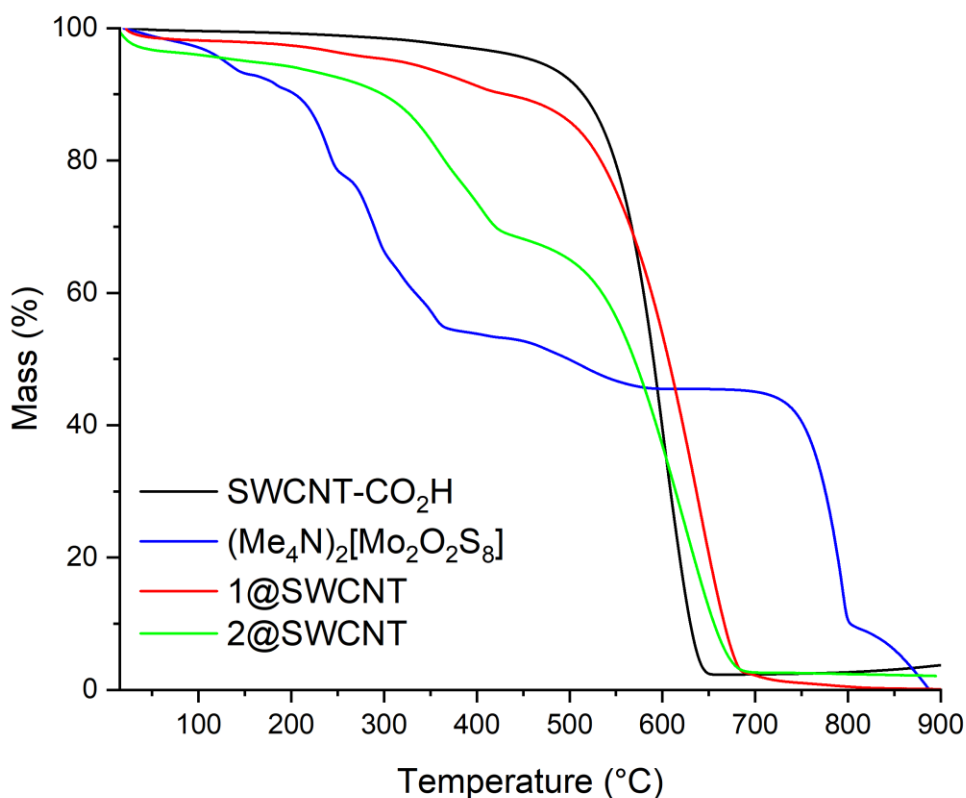
**Figure S4:** Moles of H<sub>2</sub> detected by GC plotted against theoretical moles of H<sub>2</sub> produced by the amount of charge passed. Data for 1@SWCNT (top) and 2@SWCNT (bottom).

## Thermogravimetric analysis

Thermogravimetric analysis was carried out on TA Instruments SDT Q600 (samples containing chalcogens) and a TA Instruments TGA 5500 for the carbon nanotubes. Measurements were recorded both in Ar (Fig S5) and O<sub>2</sub> (2%)/Ar mixture (Fig S6).



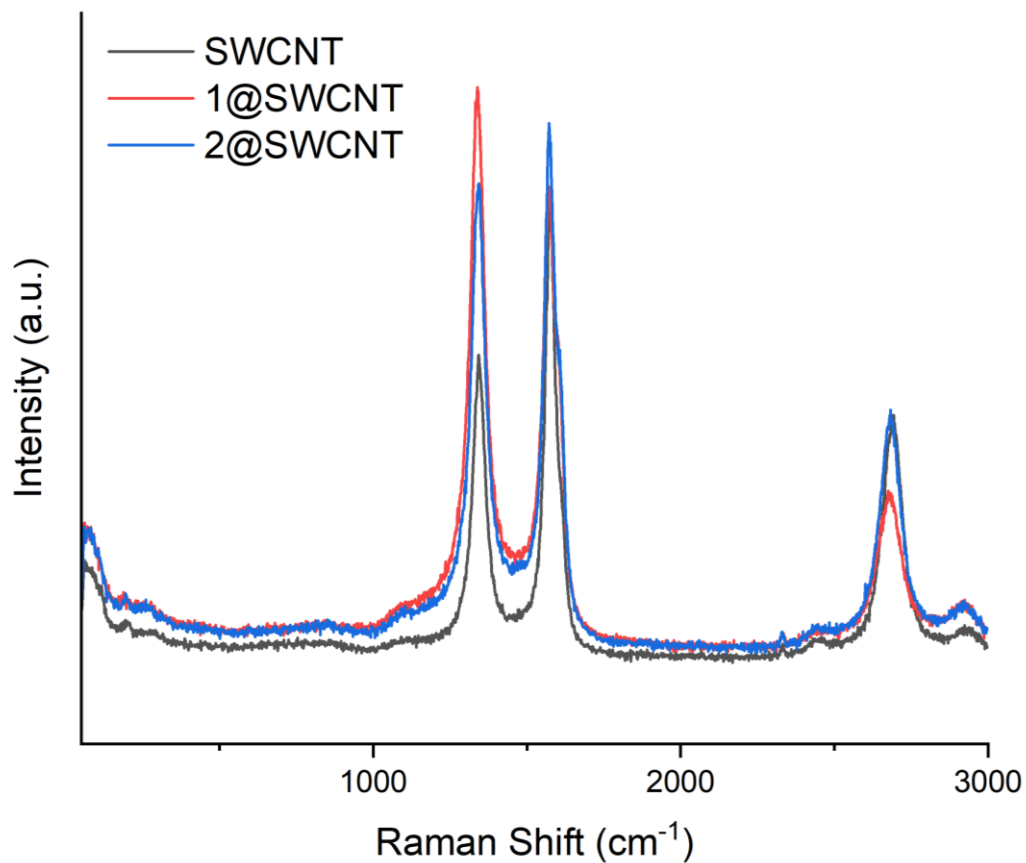
**Fig S5:** Thermal analysis of the composite materials 1/2@SWCNT and 1 under Ar atmosphere. Initial mass lost up to 100°C is attributed to adsorbed moisture and solvent. Beyond this, the loss of organic components (namely NMe<sub>4</sub><sup>+</sup>) occurs, up to approximately 300°C. Beyond this, the samples begin to diverge slightly, which is predominantly due to the mass difference of the respective chalcogens before again converging towards 900°C, as all the volatile components have been lost, demonstrating the analogous nature of the materials.

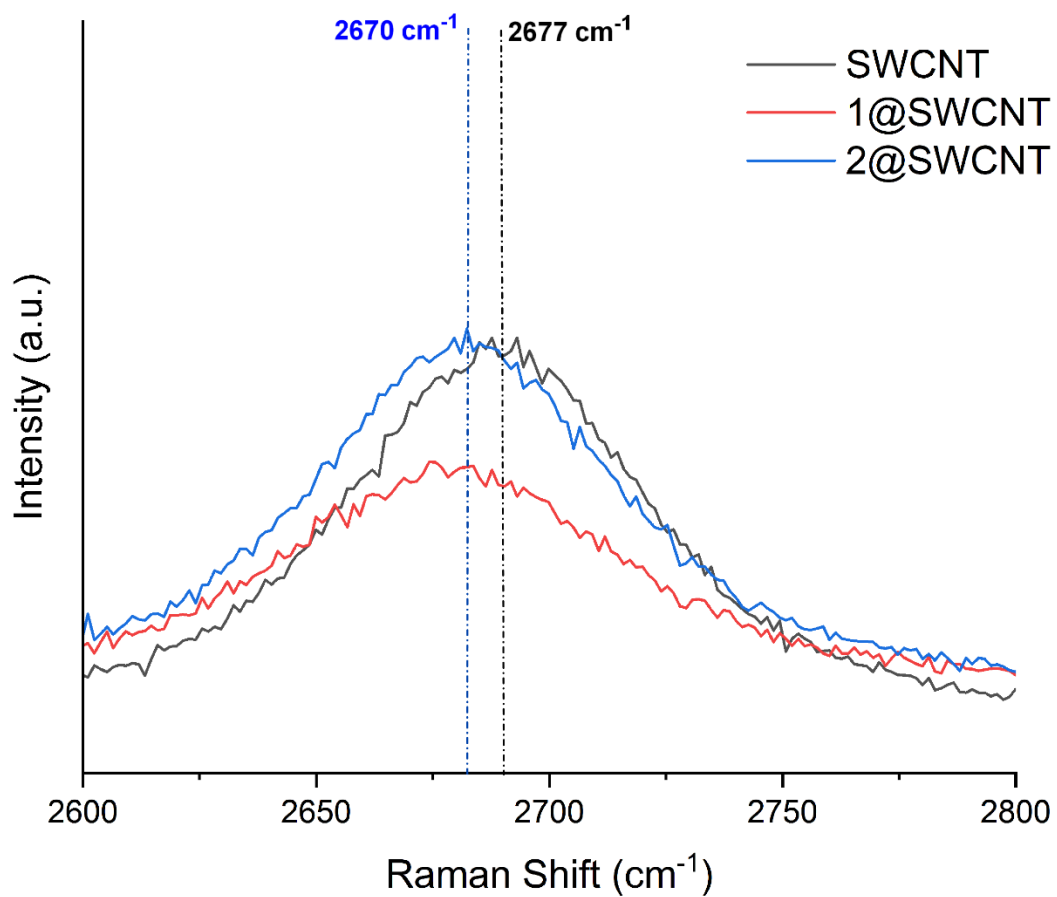
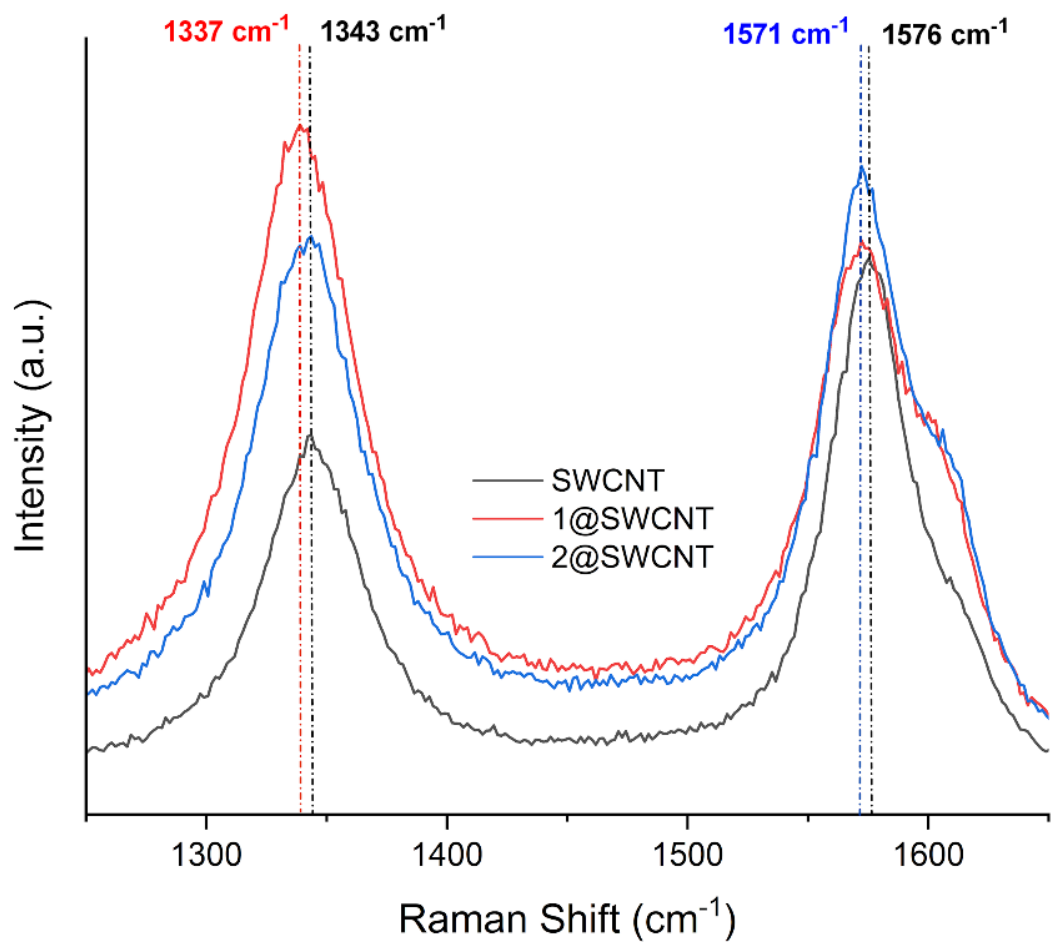


**Figure S6:** Thermal analysis of the carbon nanotubes (as received, black line), the dimeric Mo species **1** (blue line), and the composite material **1@SWCNT** (red line). The percentage mass of the composite material remaining above 695°C was used to calculate the catalyst loading, as the percentage of mass remaining allows us to establish the moles of molybdenum (as MoO<sub>3</sub>) present in the sample. Thermal analysis of material **2@SWCNT** (green line). Determination of catalyst loading was done in an analogous manner to material **1@SWCNT**. Above 800°C, the samples containing SWCNTs can potentially reabsorb upon reaction with oxygen forming less volatile species, hence these samples do not always converge. The Mo containing samples can react with oxygen to form species that exist in equilibrium, eg. MoO<sub>2</sub>, MoO<sub>3</sub> etc. and the presence of additional oxygen can influence this equilibrium in different ways depending on the relevant concentrations.

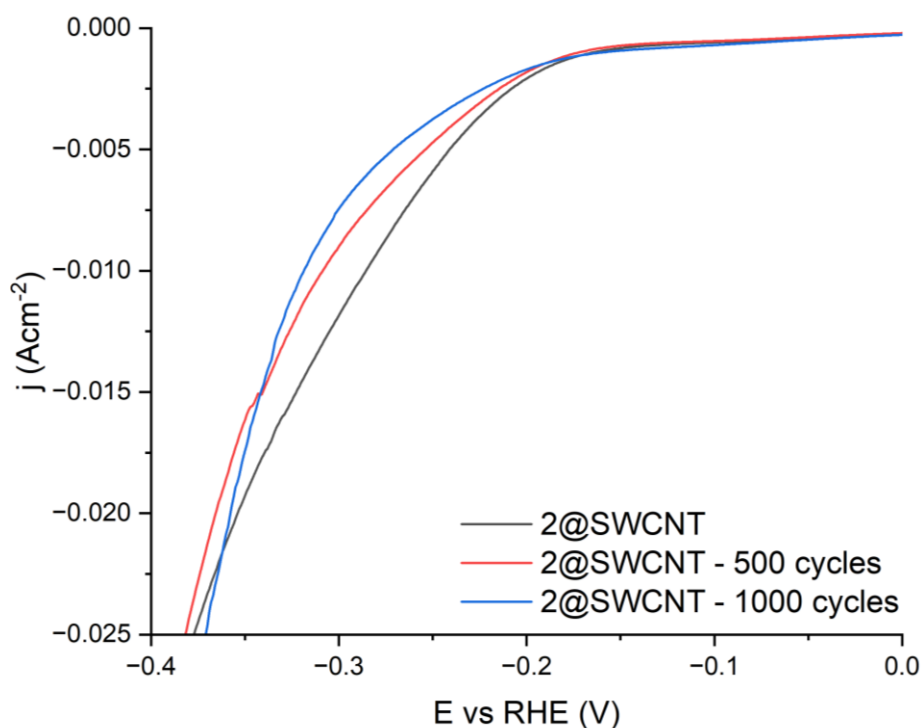
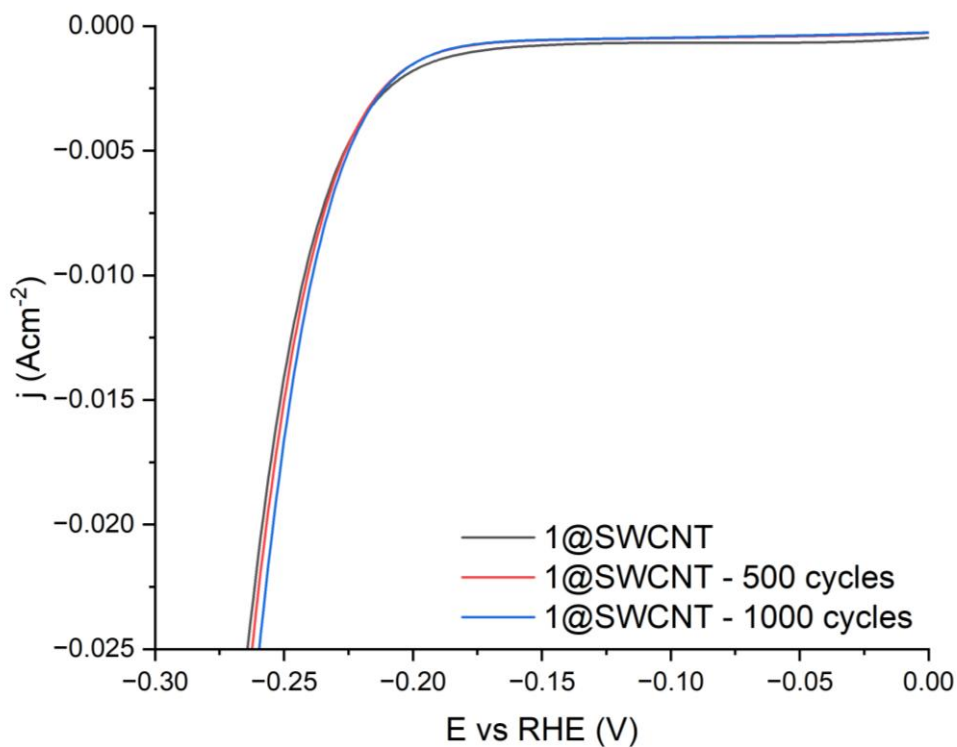
## Raman Spectroscopy

Raman spectra were recorded on a Horiba Jobin–Yvon LabRam HR800 equipped with a 532 nm laser. An aperture size of 100  $\mu\text{m}$  and a 10% filter was used in order to prevent sample degradation.

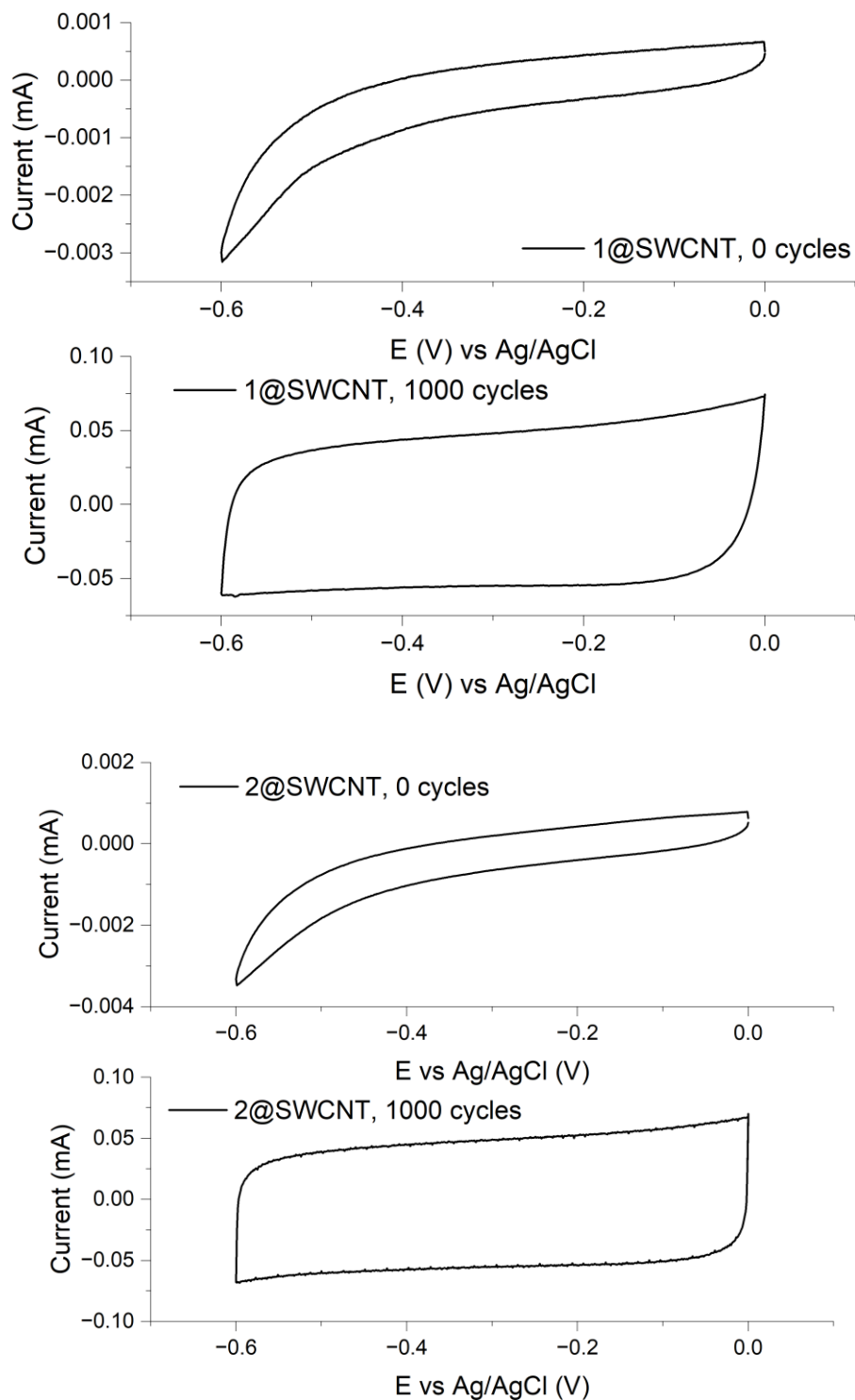




**Figure S7:** Raman Spectra recorded for SWCNT-CO<sub>2</sub>H and the composite materials 1/2@SWCNT. The 4 regions of significance are ~100-400 cm<sup>-1</sup>, corresponding to the radial breathing mode (RBM) of the SWCNTs, demonstrating the materials do not lose their cylindrical structure upon the heterogenization of the molecular species. It also serves to confirm the nanotubes used are SWCNTs, as MWCNTs have much weaker RBM signals and DWCNTs have split RBM peaks. The D band at ~1340 cm<sup>-1</sup> is a phonon disorder band caused by defects which break the graphene plane of symmetry, which is generally taken to increase in intensity with doping concentration, in addition to a shift of 6 cm<sup>-1</sup>. Such shifts are characteristic of surface processes. This corroborates our other characterisation data stating the material 1@SWCNT has the highest catalysts loading. The G band at ~1750cm<sup>-1</sup> which is associated with vibrations along the axis of the nanotube, and finally G' band at 2675 cm<sup>-1</sup>, which is a resonance band of the D band which also demonstrates a shift of 7 cm<sup>-1</sup>. The increasing prominence of the G band indicates the metallic nature of the SWCNTs and displays both an increase in intensity and a shift of 5 cm<sup>-1</sup>.<sup>3,4</sup> Most importantly, the absence of characteristic Raman peaks of C-S (~616, 660 cm<sup>-1</sup>) or C-O/C=O (~1770 cm<sup>-1</sup>) indicate the absence of both forms of bonding where it would be the case if we had coordinative interaction between the molecular catalyst and the CNT. Hence, the molecular species are adsorbed to the surface of the CNTs without forming covalent bonds.

**Additional Electrochemical Data**

**Fig S8:** LSV data recorded at 500 cycle intervals for **1/2@SWCNT**, to establish long term stability of the species. **1@SWCNT** showed shifts of 1 - 4 mV, while **2@SWCNT** showed shifts of 5 - 10 mV respectively.

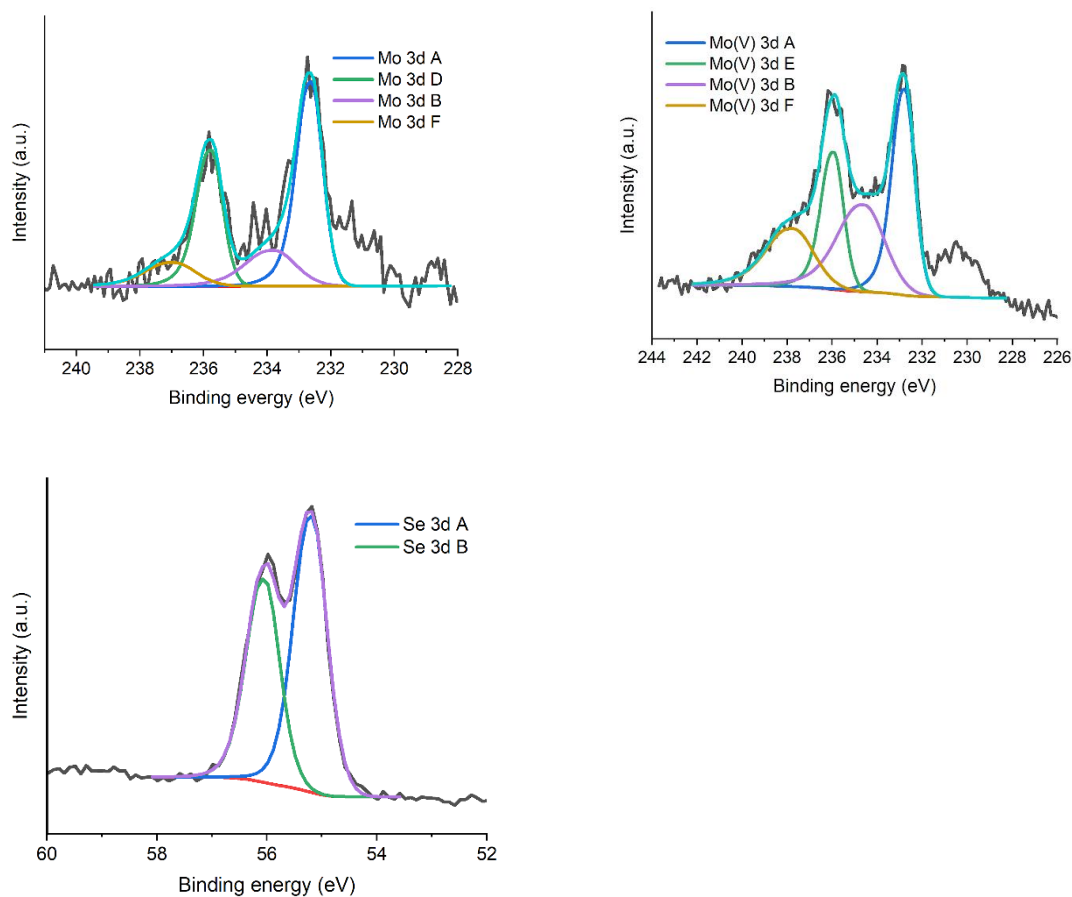


**Fig S9:** CV measurements before and after the accelerated cycling experiments, recorded in organic media as described above. The absence of additional peaks shows no significant structural or chemical changes occurred during the electrocatalytic process.



## XPS

XPS were performed on a Kratos AXIS Supra+ equipped with a dual source X-ray filament (Ag/Al). Preliminary XPS studies that confirmed the relevant oxidation states of the metal and chalcogen centres. The XPS spectra derived from the surface included a Mo and Se 3d<sub>5/2</sub> spectrum of 232.4 and 55.4 eV binding energy, respectively, which are in good agreement to previously reported Mo(V) and Mo-Se species<sup>5,6</sup>



## References

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