Supplementary Information for

Facile fabrication of conductive MoS$_2$ thin films by sonication in hot water and evaluation of their electrocatalytic performance in the hydrogen evolution reaction

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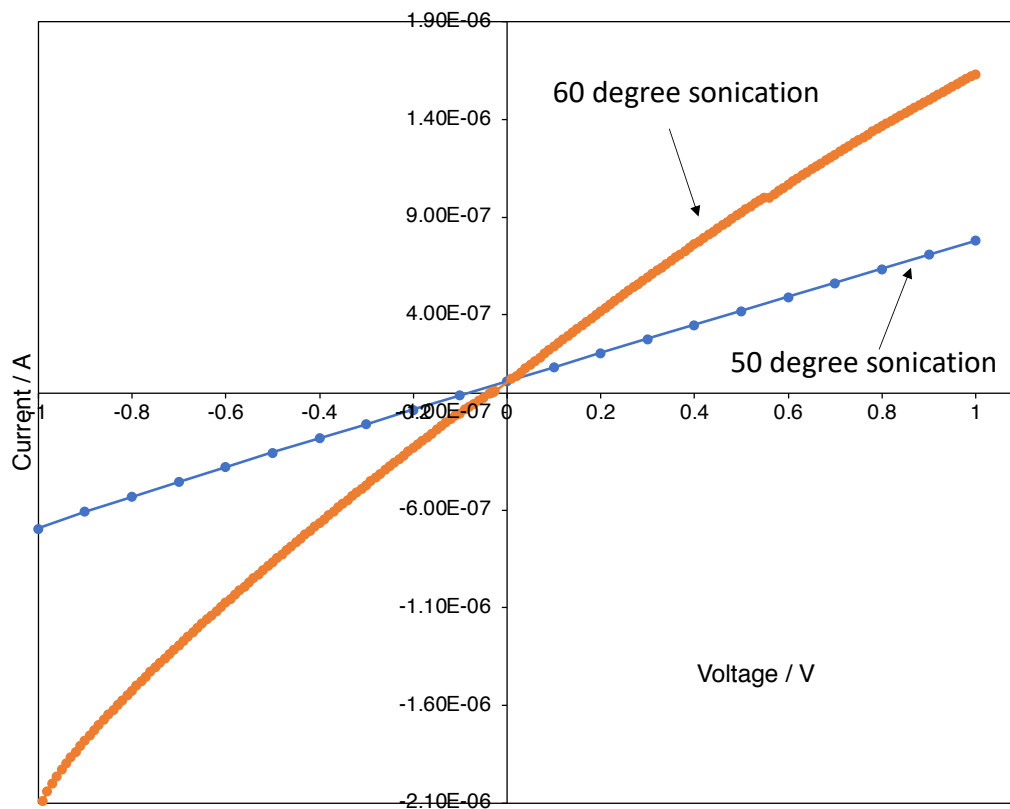# Two-probe conductivity measurement comparison

Figure S1: I *vs.* V graph comparison of two-probe conductivity measurement of MoS$_2$ samples exfoliated at 50 °C and 60 °C in water. Conductivity measurements are carried out using a Keithley 2450 Source Meter at room temperature. Geometry of the film is fabricated as previously reported in ref. 1.
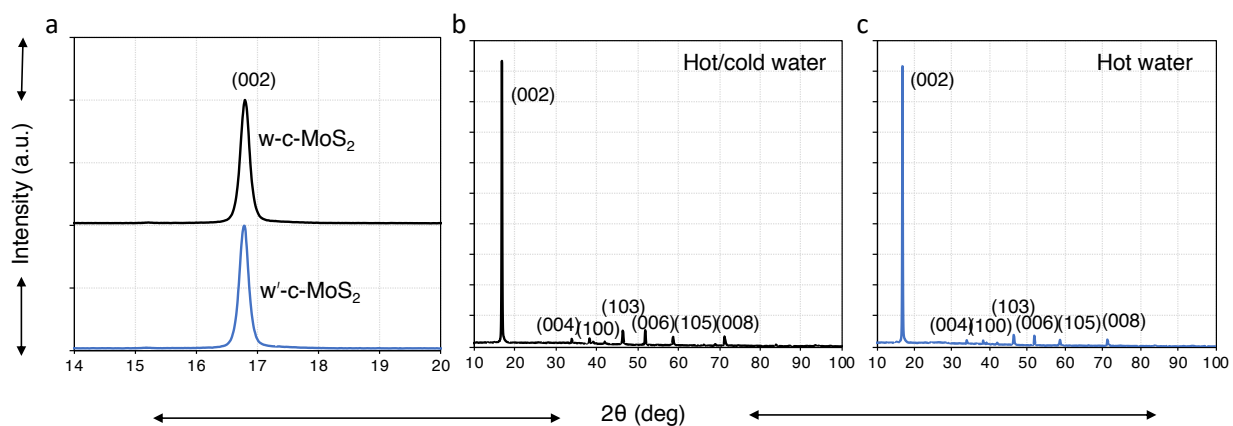
X-ray diffraction

Figure S2: XRD of water exfoliated c-MoS$_2$ solid films. There is no peak for MoO$_2$ (2θ ~25 deg). The rest of the features match well to 2H-MoS$_2$. No other discernible peaks remain unidentified indicating that the crystalline part of the sample is 2H-MoS$_2$. There is a slight shift of the (002) peaks compared to bulk MoS$_2$ for all the water exfoliated samples due to the effect of doping. (a) Comparison between the high-resolution XRD (002) peaks near 16° of water exfoliated conductive MoS$_2$ prepared both ways, showing their crystallographic similarity; (b) XRD of conductive MoS$_2$ exfoliated using hot and cold-water sonication, and (c) XRD of conductive MoS$_2$ exfoliated using only hot water sonication.
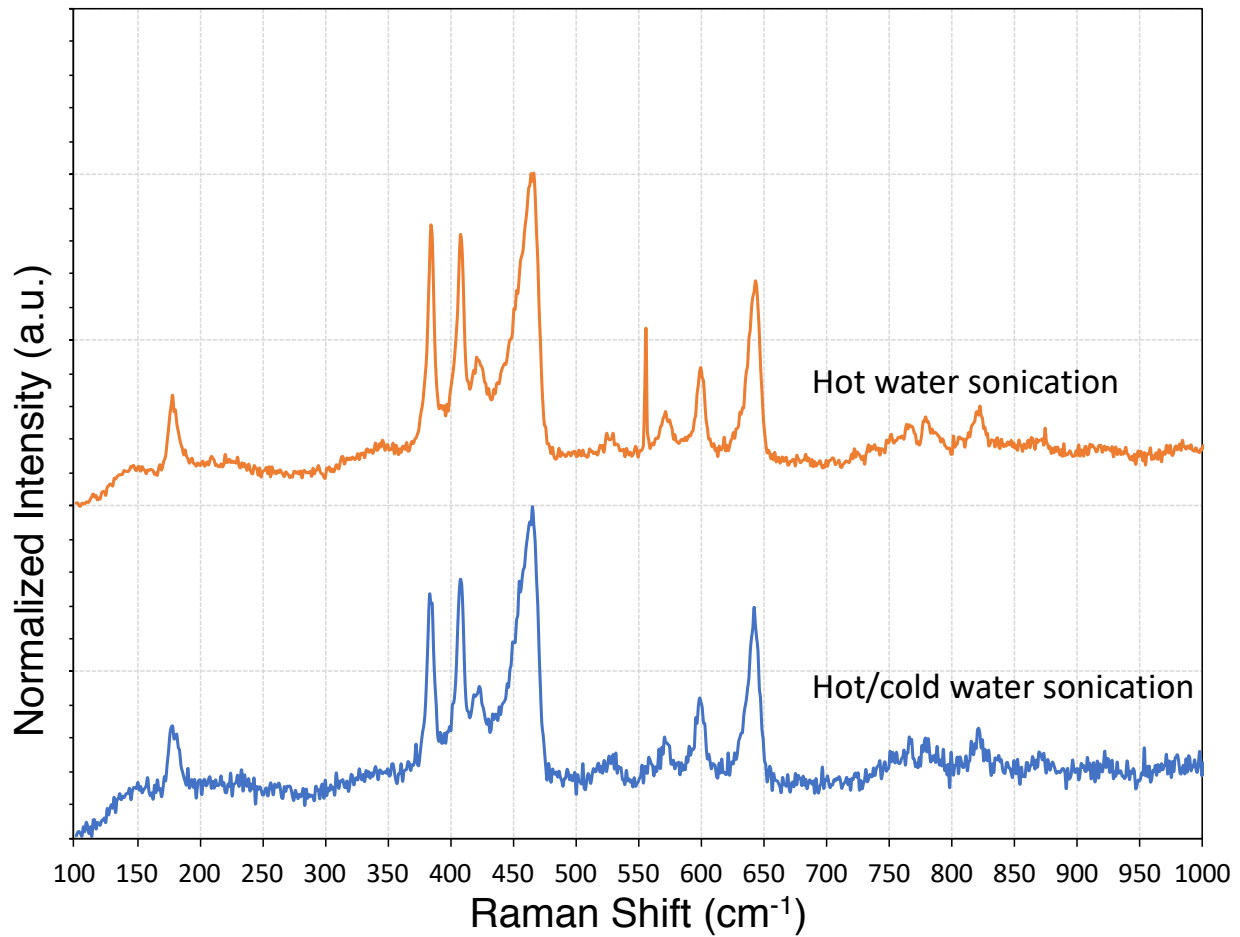
Raman spectroscopy

Figure S3: Raman spectra of water exfoliated conductive MoS_2 prepared in two ways. The samples were illuminated by a 633 nm laser at 1% power. The peak intensity is normalized based on the highest peak of the spectra (466 cm^{-1}). Blue color represents conductive MoS_2 exfoliated using hot and cold-water sonication, and orange color is for conductive MoS_2 exfoliated using only hot water sonication samples.

High resolution S 2p XPS of pristine semiconducting, water exfoliated, and peroxide exfoliated MoS₂
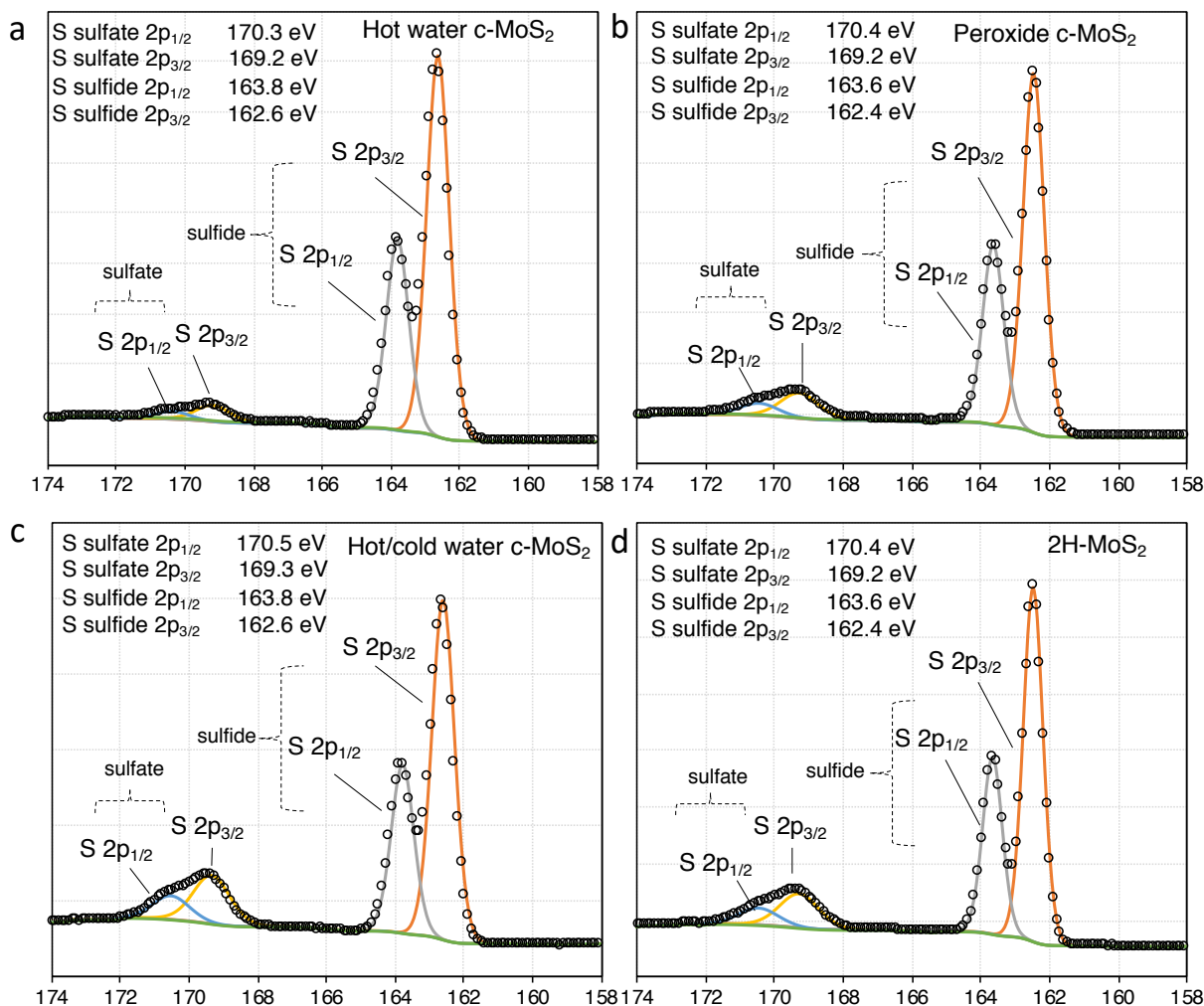

Figure S4: XPS high resolution spectra of as-prepared conductive MoS₂ samples, either by hot water sonication only, or by hot water sonication followed by cold water sonication, or by sonication in dilute peroxide, and of semiconducting 2H-MoS₂ samples. Spectra are S 2p for (a) exfoliated conductive MoS₂ using only hot sonication procedure; (b) exfoliated conductive MoS₂ using aqueous peroxide sonication procedure; (c) exfoliated conductive MoS₂ using hot and cold sonication procedure; and (d) exfoliated semiconducting 2H-MoS₂.

Colorimetric experiment

Experiment details:

The amount of H_2O_2 was measured using the diethyl-p-phenylenediamine (DPD) method in a Smart 3 colorimeter from LaMotte. The low range protocol with a working range of 0.00 -1.50 ppm was used to quantify the amount of hydrogen peroxide produced in water during sonication. A 10 ml volume of sample was added to a clean reagent tube (Figure S5a). The tube was inserted in the colorimeter to set the blank reading for the measurement. The tube was removed and 4 drops of H_2O_2 reagent 1 were added to the sample. Then, one H_2O_2 low range tablet was added to the sample and the tablet was crushed using a glass rod followed by mixing for approximately 30 s. The appearance of a pink color in the samples confirms the presence of H_2O_2. However, the final measurement was performed after 5 minutes to ensure full color development. The testing procedure works via the reaction of released iodine with DPD. In presence of excess potassium iodide, H_2O_2 reacts with potassium iodide to generate iodine. This released iodine reacts with DPD to generate a pink color proportional in intensity to the amount of iodine.
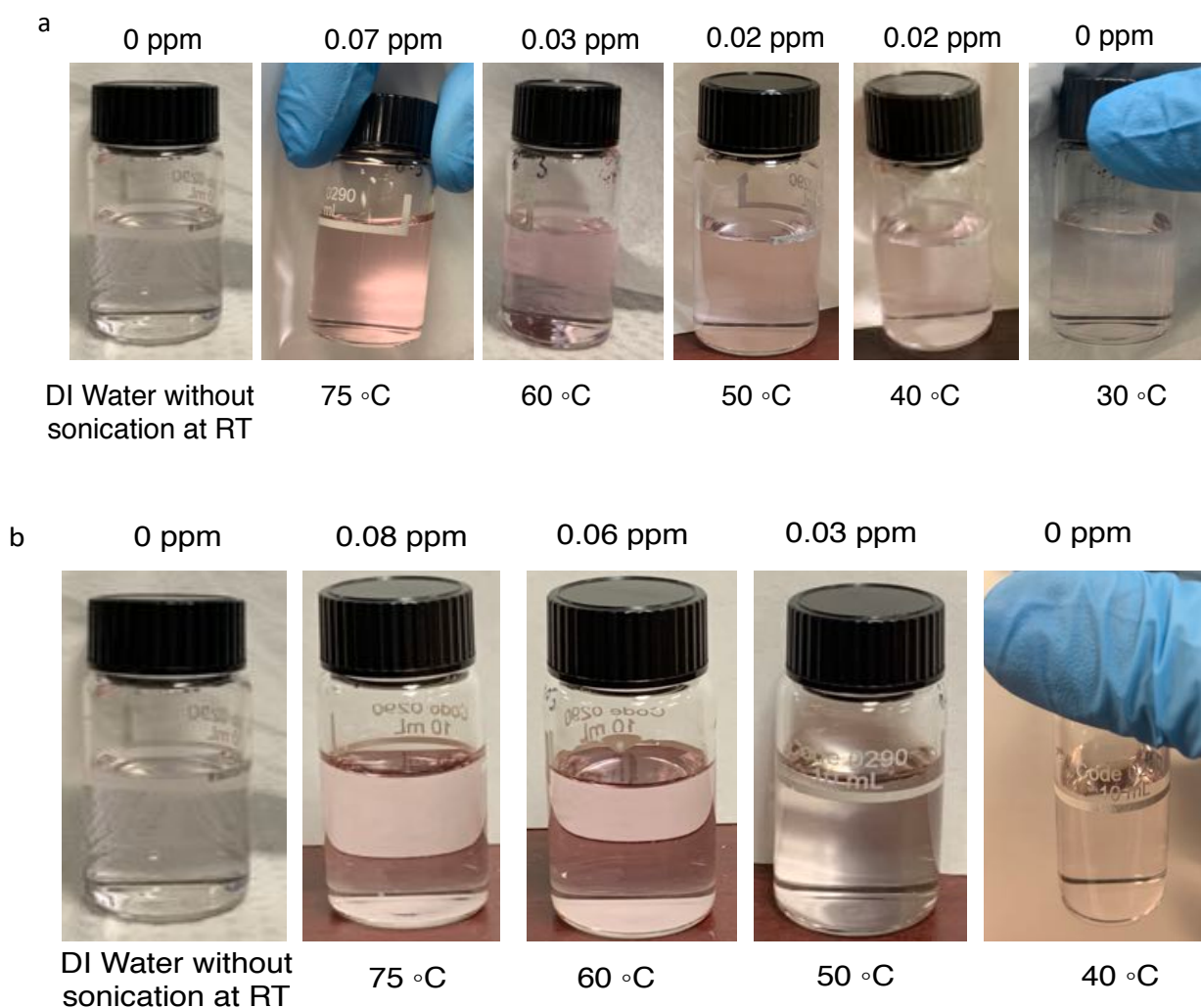
Figure S5: Colorimetric test for H_2O_2 formation in water at different temperatures and for two different sonication frequencies. All experiments were carried out in DI water. Sonication time for all samples was 3 hours 40 minutes. Temperature was controlled during sonication by using the built-in thermostat and heater of the sonicator. A cooling coil running with tap water was immersed into the sonicator bath for cooling. (a) H_2O_2 formation using 37 kHz sonicating frequency; and (b) H_2O_2 formation using 80 kHz sonicating frequency.

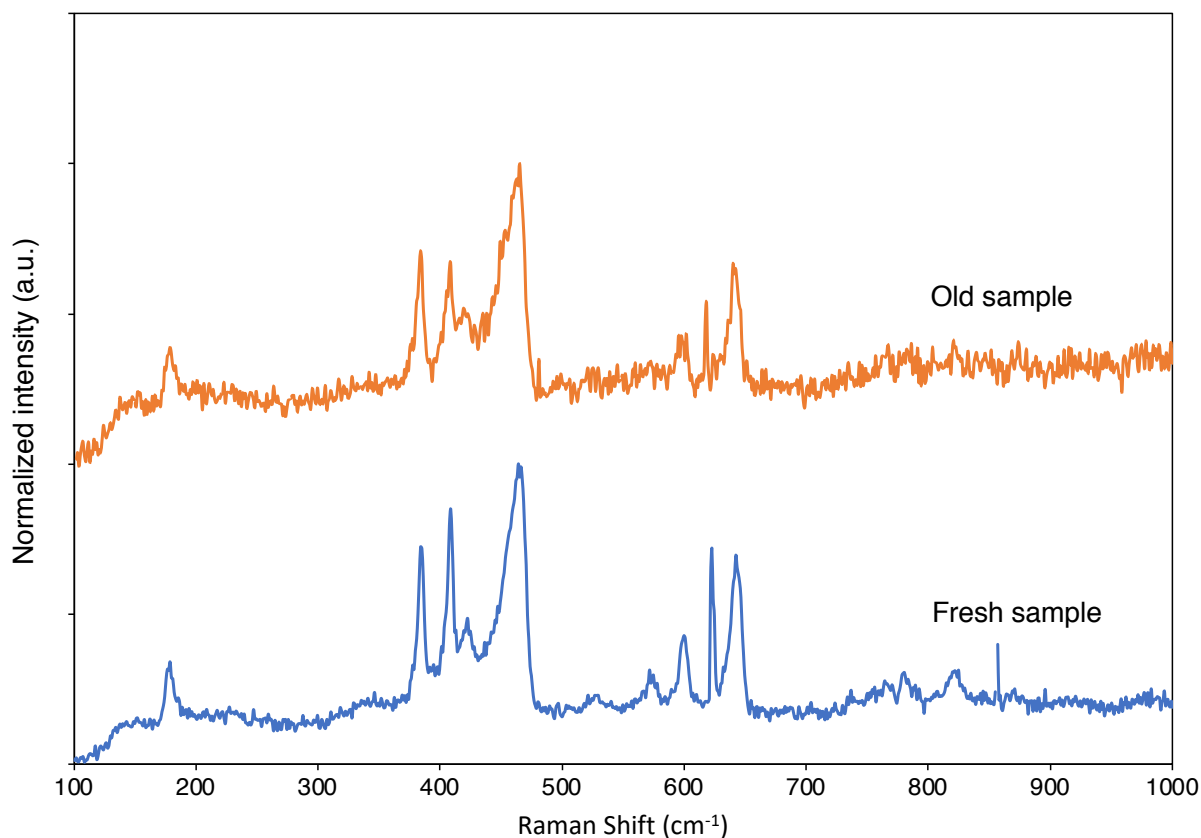# Raman spectroscopy of fresh and old water exfoliated MoS₂ sample

Figure S6: Raman spectra of old and fresh water exfoliated conductive MoS_2. The samples were illuminated by a 633 nm laser at 1% power. The peak intensity is normalized based on the highest peak of the spectra (466 cm^{-1}). Fresh sample meaning Raman spectra has taken immediately after exfoliating conductive MoS_2 in a same day and old sample refers to the Raman spectra which has taken 21 days after exfoliating conductive MoS_2. Old sample has kept in glass petri dish at ambient conditions for 21 days.

Electrochemical surface area of MoS₂ samples

Figure with axes: x-axis "Scan rate / mV/s" (0 to 100), y-axis "Current density / mA/cm²" (0.02 to 0.12). Three data series:
- Peroxide MoS₂, 1.68 mF/cm² (orange)
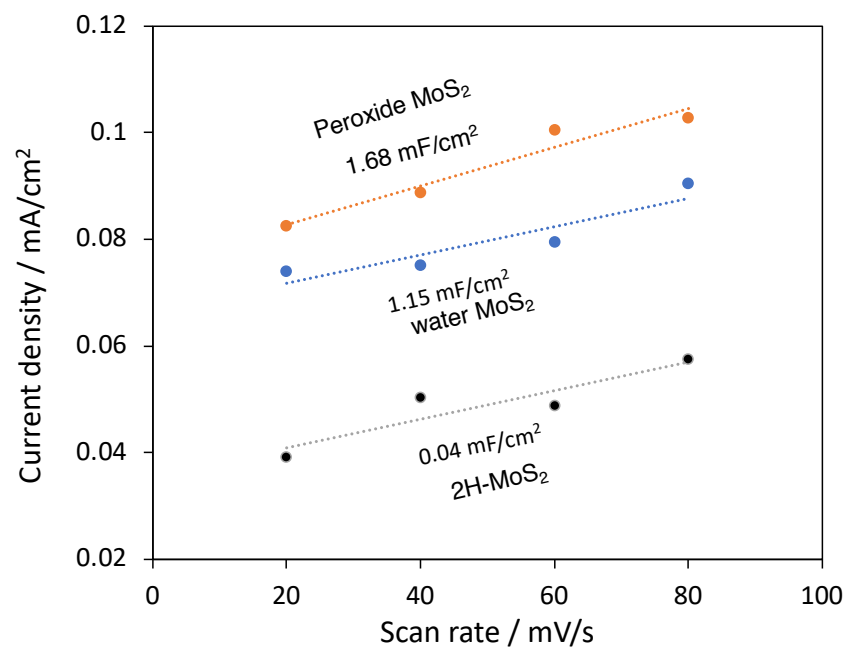- 1.15 mF/cm², water MoS₂ (blue)
- 0.04 mF/cm², 2H-MoS₂ (black)

Figure S7. Capacitance current density vs different scan rates.

High resolution XPS of oxidised semiconducting, water and peroxide exfoliated MoS$_2$ samples
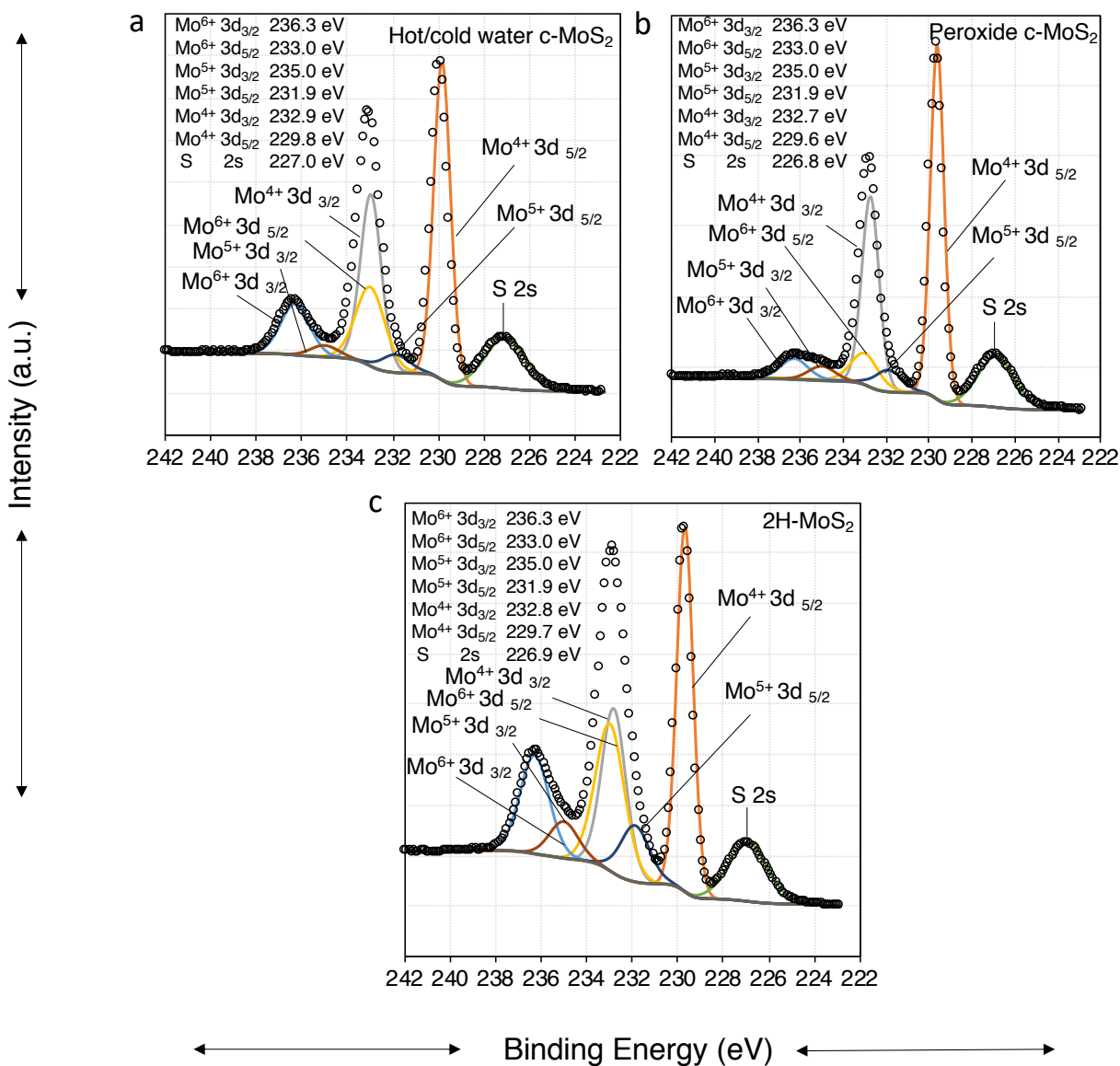

Figure S8: XPS high resolution spectra of oxidised water induced conductive MoS$_2$, peroxide induced conductive MoS$_2$ and semiconducting MoS$_2$ samples. Spectra are Mo 3d for (a) exfoliated conductive MoS$_2$ using hot and cold sonication procedure (b) exfoliated conductive MoS$_2$ using aqueous peroxide sonication procedure; and (d) exfoliated semiconducting 2H-MoS$_2$

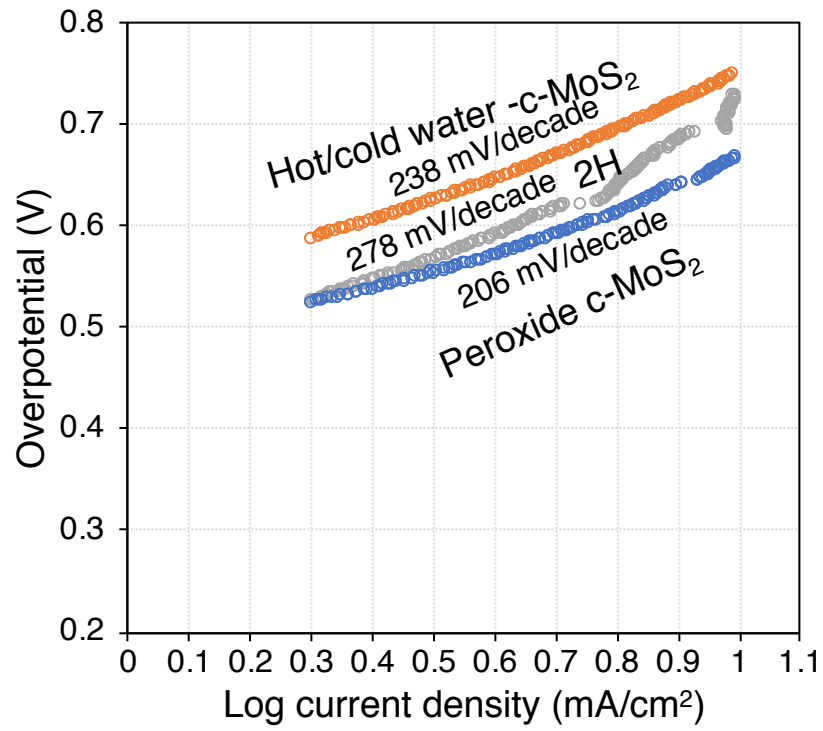# Tafel plot of oxidised MoS$_2$ samples

Figure S9: Polarization graph of oxidised MoS$_2$ samples.
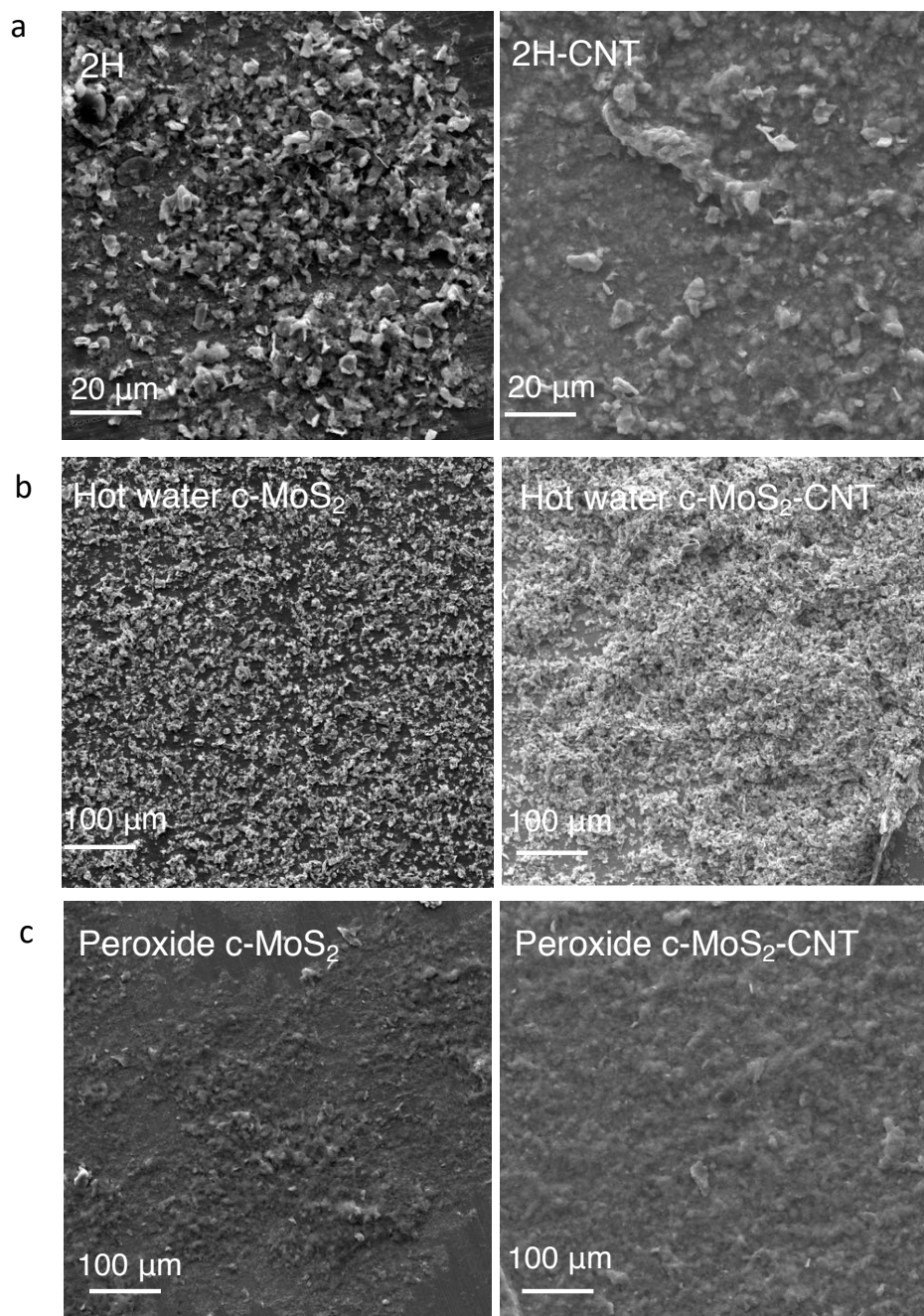
Surface morphology of MoS₂ with carbon nanotubes

Figure S10: SEM images of different pristine MoS$_2$ (left side) and MoS$_2$-SWCNT composite pristine materials (right side). Materials are (a) pristine semiconducting 2H-MoS$_2$. Scale bar is 20 µm; (b) Pristine hot and cold water exfoliated c-MoS$_2$. Scale bar is 100 µm; and (c) peroxide exfoliated c-MoS$_2$. Scale bar is 100 µm

Polarization value of carbon nanotube-MoS$_2$

Table S1: Polarization table of SWCNT-MoS$_2$ samples.

Material	Overpotential (mV)	Tafel Slope (mV/decade)
Semiconducting 2H-MoS$_2$	755	323
Water exfoliated c-MoS$_2$	759	304
Peroxide exfoliated c-MoS$_2$	716	282

High resolution XPS of semiconducting, water and peroxide exfoliated MoS₂ HER samples
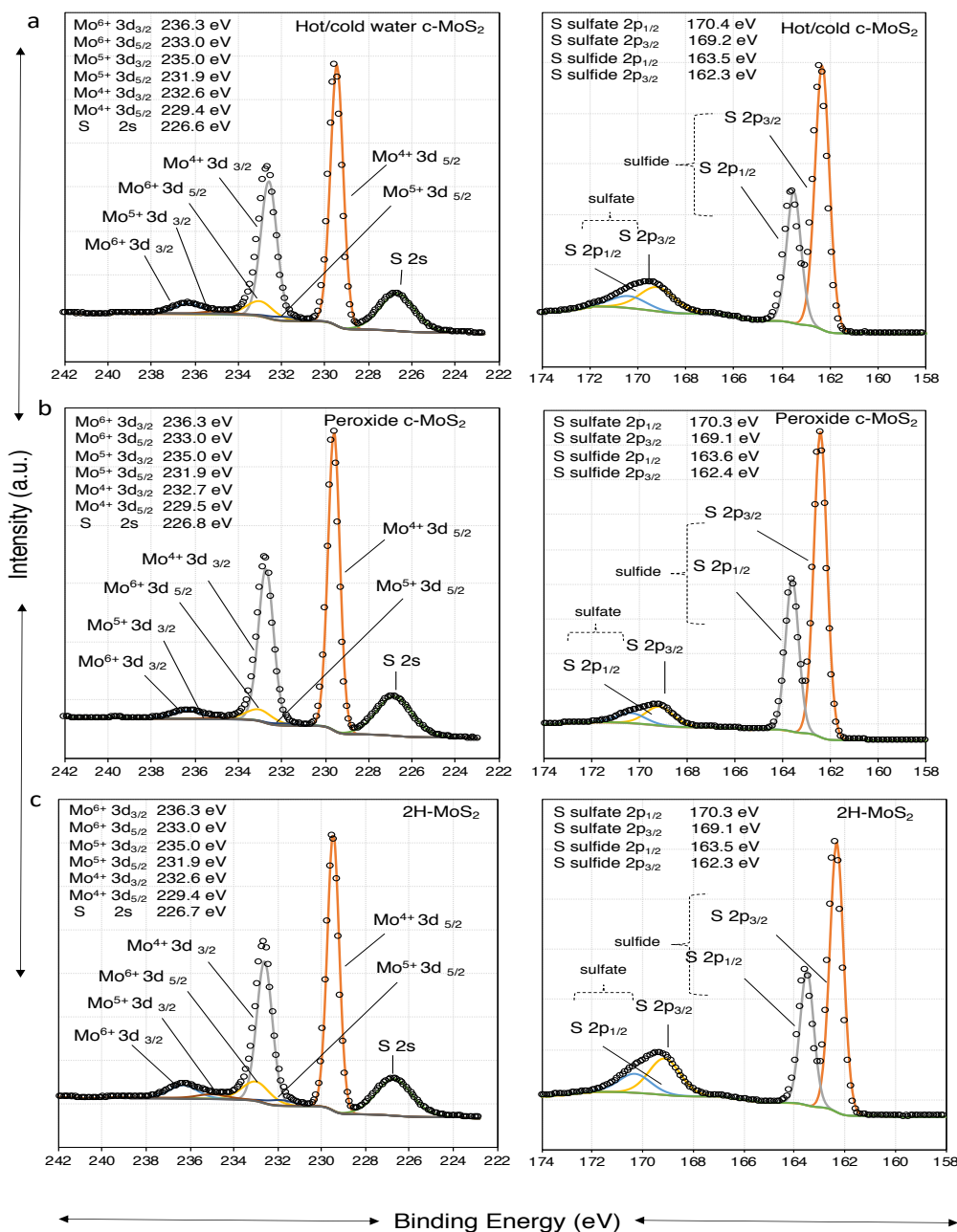

Figure S11: XPS high resolution spectra of HER samples. Spectra are Mo 3d and S 2p in (a) exfoliated conductive MoS₂ using hot and cold sonication procedure; (b) exfoliated conductive MoS₂ using aqueous peroxide sonication procedure; and (c) exfoliated 2H-MoS₂.
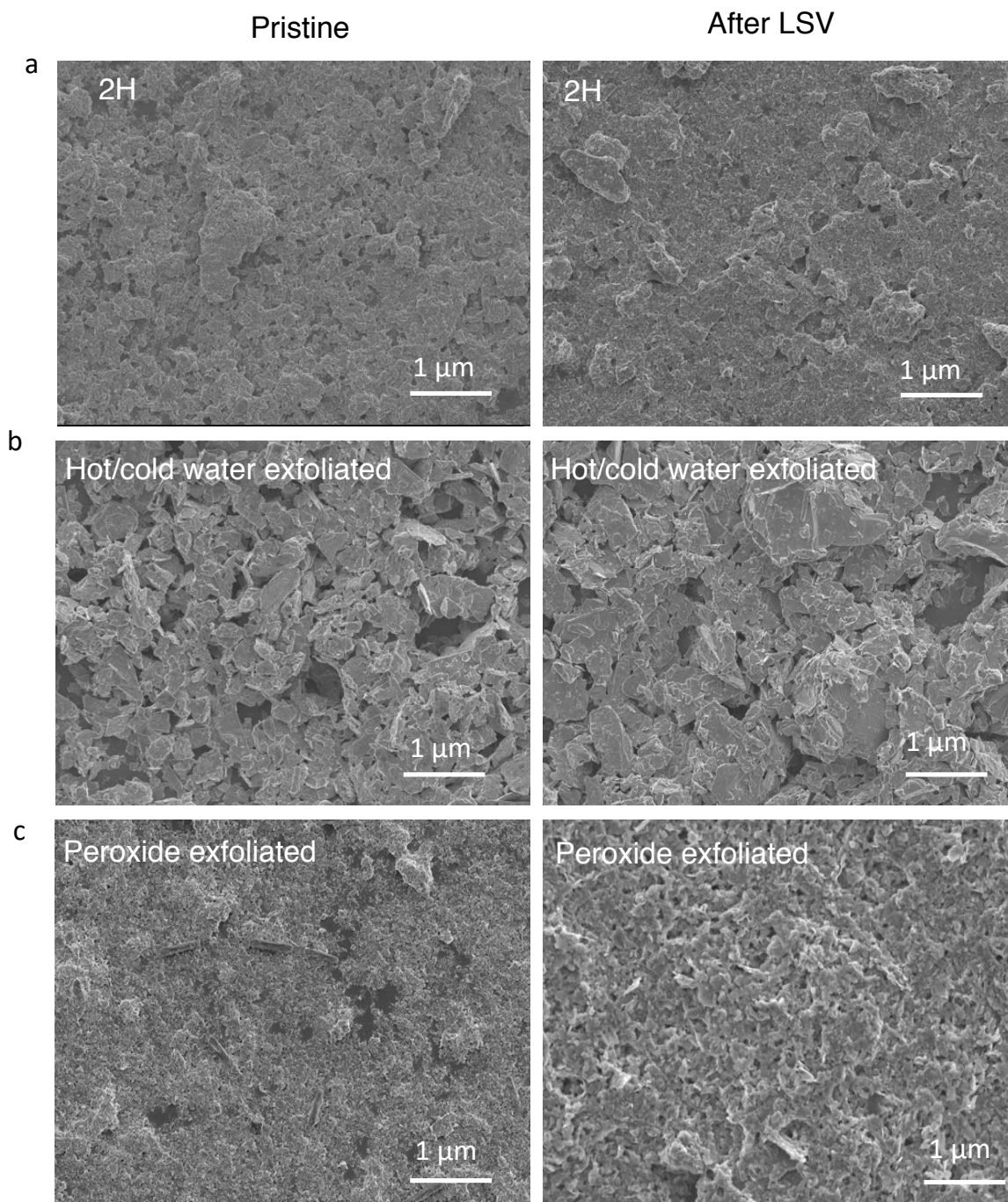
Surface morphology before and after HER

Figure S12. High resolution SEM images of different MoS_2 materials before (left side) and after linear sweep voltammetry (right sides). Samples are a) pristine semiconducting 2H-MoS_2; (b) Pristine hot and cold water exfoliated c-MoS_2; and (c) peroxide exfoliated c-MoS_2. All scale bars are 1 μm.
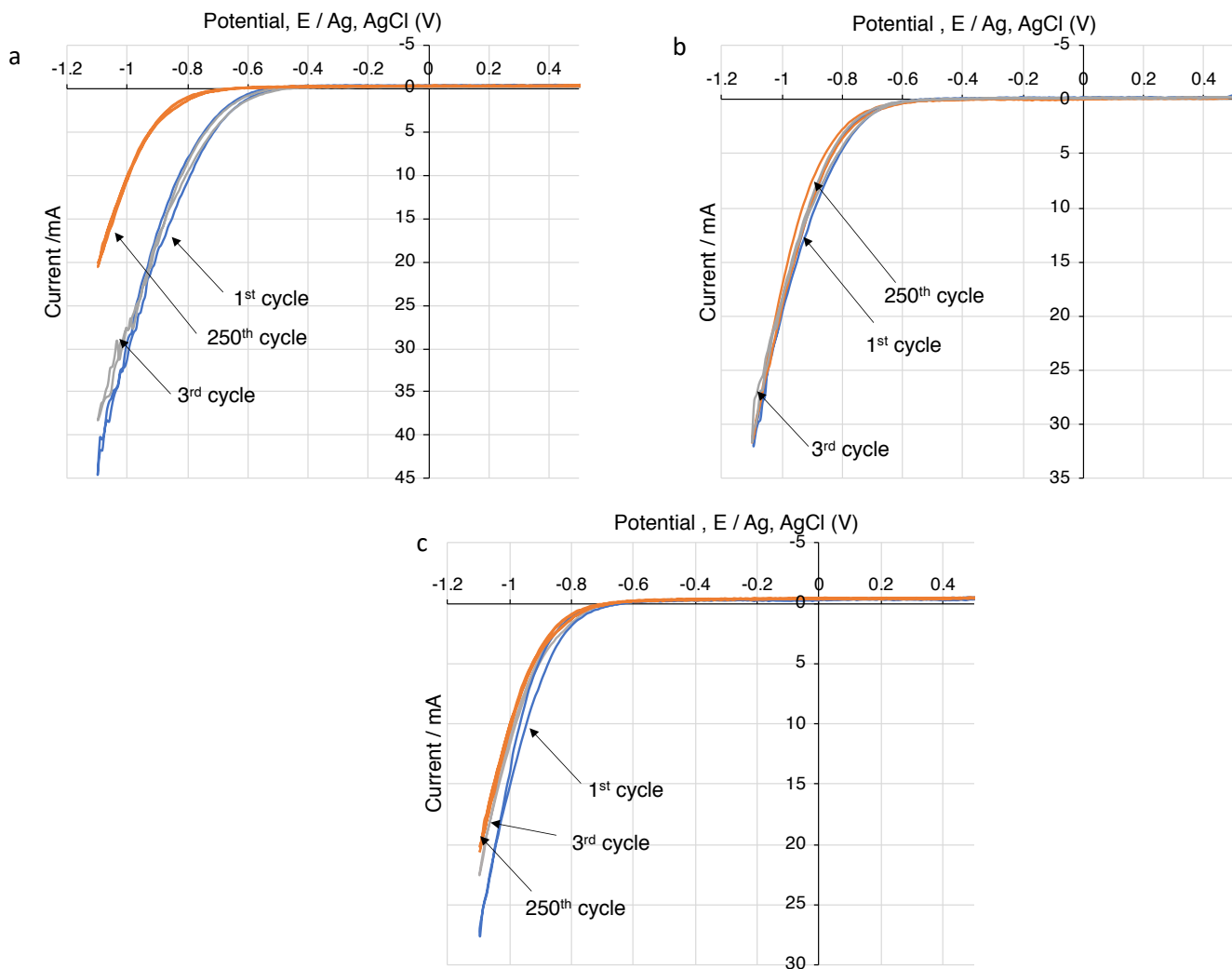
Cyclic voltammetry of doped MoS₂

Figure S13. Cyclic voltammetry of different MoS$_2$ materials. Samples are a) Peroxide exfoliated c-MoS$_2$, (b) Pristine hot and cold water exfoliated c-MoS$_2$; and (c) Pristine semiconducting 2H-MoS$_2$. All are the reduction peaks due to the hydrogen evolution.

Stability of doped MoS$_2$

Table S2. Polarization values before and after cycling (250 cycles of cyclic voltammetry, see Figure S10) of different doped MoS$_2$ materials.

Materials	Overpotential before 1st cycle (mV)	Overpotential after 250 cycles (mV)	Tafel slope before 1st cycle (mV/decade)	Tafel slope after 250 cycles (mV/decade)
2H-MoS$_2$	773	798	333	317
Water exfoliated c-MoS$_2$	780	790	204	170
Peroxide exfoliated c-MoS$_2$	632	712	242	181

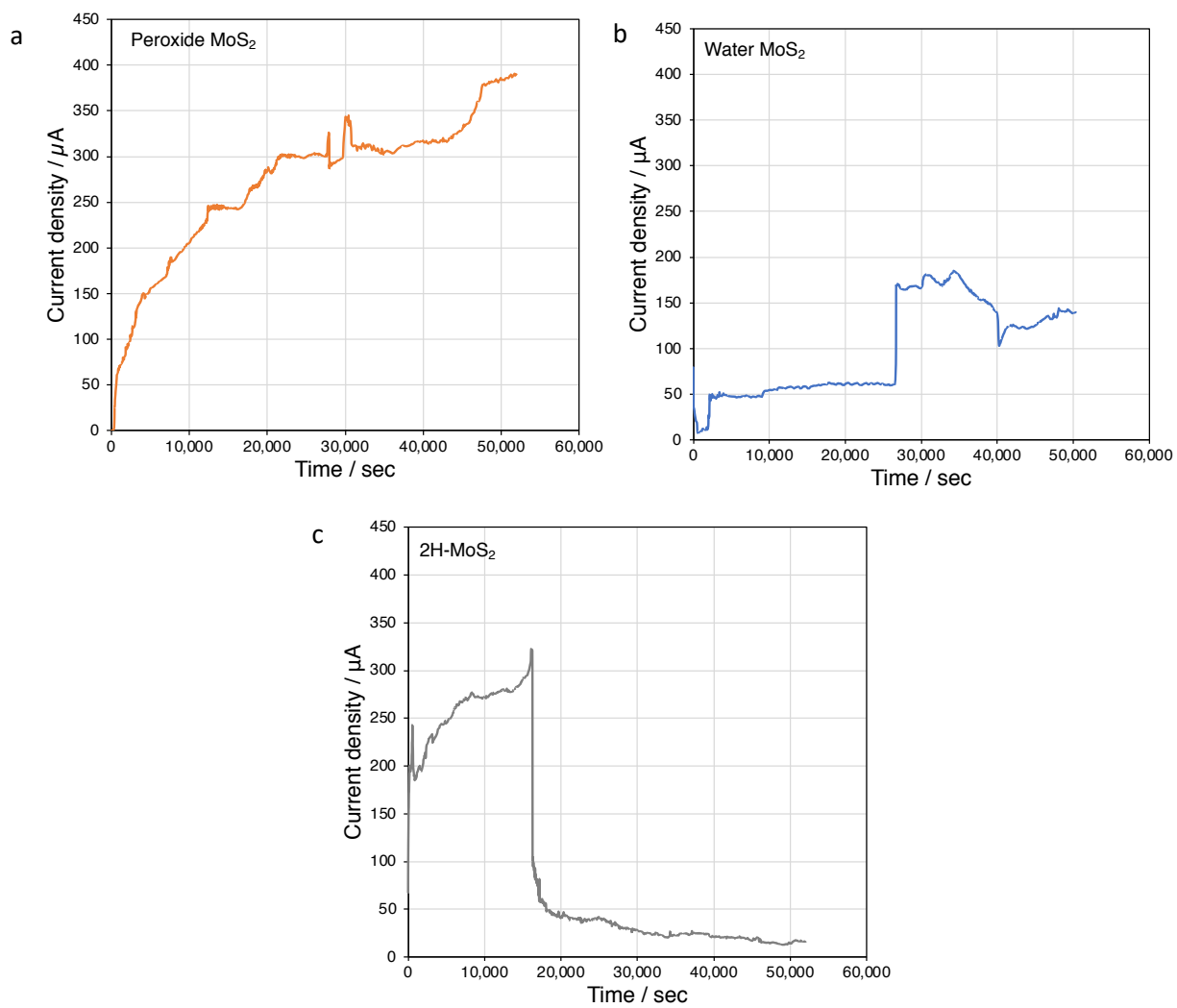# Chronoamperometry experiment of MoS₂ samples

Figure S14. Current *vs.* time plot at fixed overpotential. Samples are a) semiconducting 2H-MoS₂; (b) hot and cold water exfoliated c-MoS₂; and (c) peroxide exfoliated c-MoS₂.

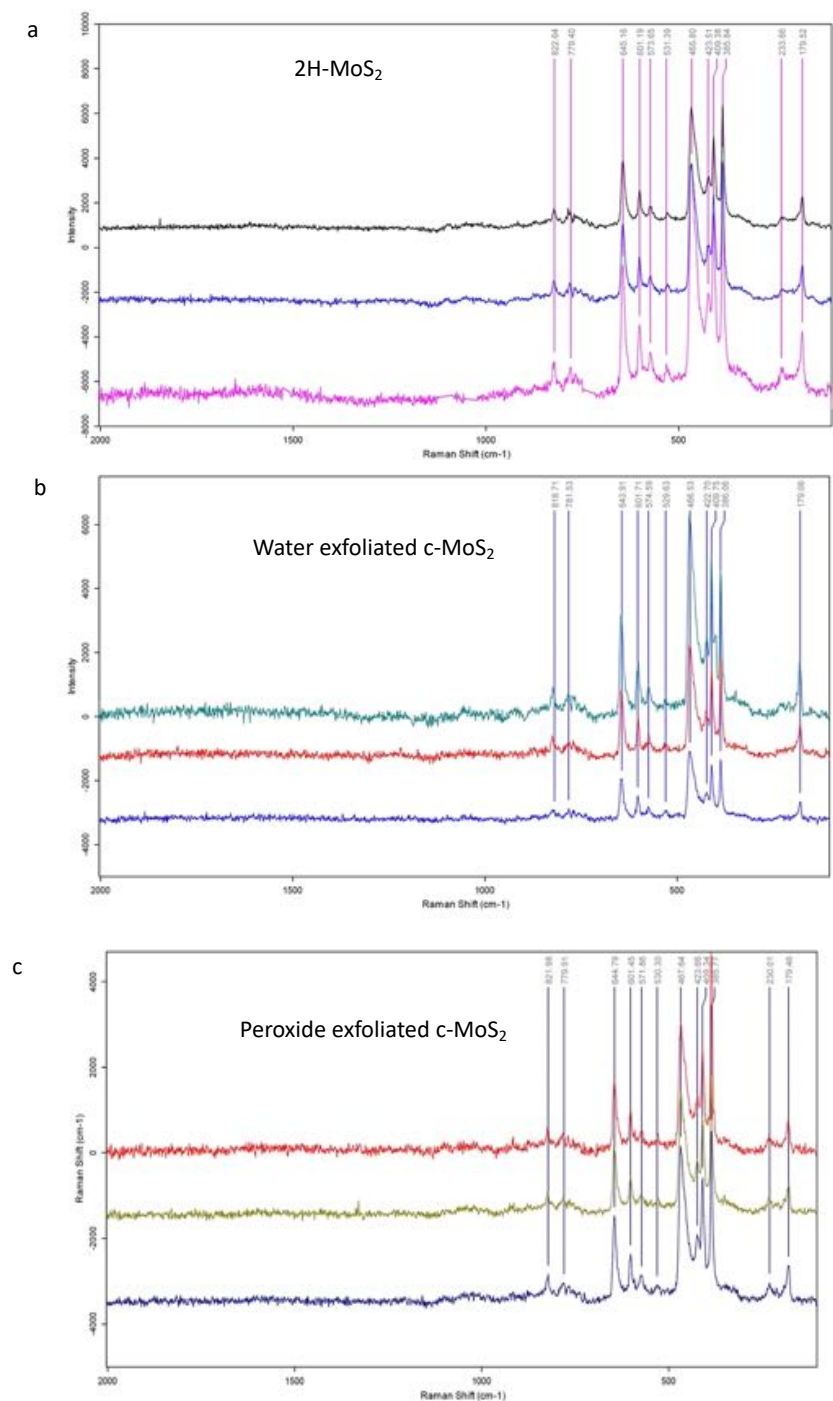# Raman spectroscopy of MoS₂ samples after chronoamperometry experiment

Figure S15: Raman spectra of (a) 2H, (b) water and (c) peroxide exfoliated conductive MoS₂. The samples were illuminated by a 633 nm laser at 1% power. The peak intensity is normalized based on the highest peak of the spectra (466 cm⁻¹). For each sample, spectra are taken in a three different spots.

Compositional changes of pristine samples and samples after completion of the chronoamperometry experiment

Table S3. Compositional changes of pristine samples ("before C.E.") and samples after completion of the chronoamperometry experiment ("after C.E.") from high resolution XPS. S to Mo atomic ratios of semiconducting 2H-MoS$_2$, water exfoliated c-MoS$_2$, and peroxide exfoliated c-MoS$_2$ samples. The atomic ratios of sulfide to molybdenum (IV) were calculated from the total atomic percentages of Mo and S in high-resolution XPS spectra of S 2p and Mo 3d. The atomic ratios of Mo (IV) relative to the total Mo content in 2H-MoS$_2$, water exfoliated c-MoS$_2$, and peroxide exfoliated c-MoS$_2$ samples were calculated by using high-resolution XPS spectra of Mo 3d.

Samples	Total Mo % (before C.E.)	Total Mo% (after C.E.)	Total S% (before C.E.)	Total S% (after C.E.)	S^{2-}/Mo^{4+} (before C.E.)	S^{2-}/Mo^{4+} (after C.E.)
2H-MoS$_2$	10.40	9	15.40	17.80	1.41	1.56
water exfoliated c-MoS$_2$	12.50	10.40	16.90	21.20	1.41	1.50
Peroxide exfoliated c-MoS$_2$	15	11.90	20.20	22.30	1.45	1.50

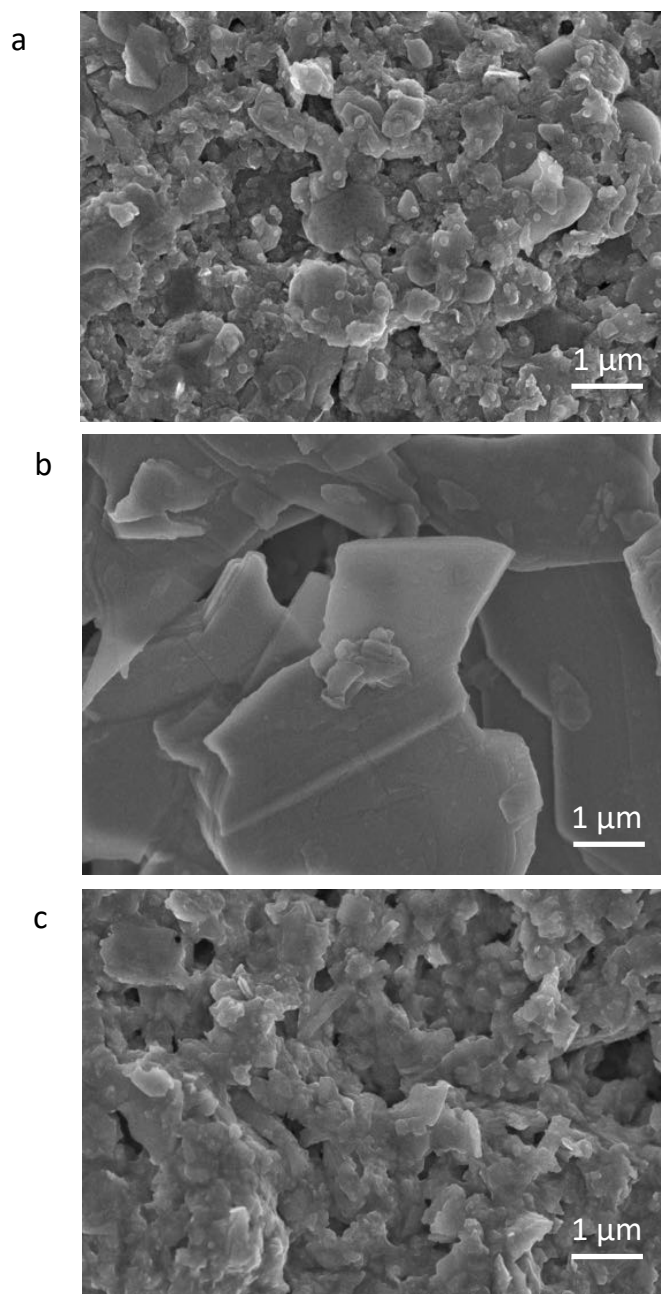# SEM of MoS$_2$ samples after chronoamperometry experiment

a

b

c

Figure S16. High resolution SEM images of different MoS$_2$ materials after completion of the chronoamperometry experiment. Samples are a) semiconducting 2H-MoS$_2$; (b) hot and cold water exfoliated c-MoS$_2$; and (c) peroxide exfoliated c-MoS$_2$. All scale bars are 1 μm.

Reference

1. D. Saha, P. R. Selvaganapathy and P. Kruse, *ACS Applied Nano Materials*, 2020, **3**, 10864-10877.