

## Photochemically Engineered Ultra-stable 1T MoS<sub>2</sub> by Flow Synthesis

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### Materials and experiments

**Materials.** The following chemicals and reagents were used without further purification: Sodium molybdate (anhydrous powder, 99.9% trace metals basis; Sigma-Aldrich), Thioacetamide (TAA) (ACS reagent, > 99%; Sigma-Aldrich), N, N-dimethylformamide (DMF; ACS for analysis; Merck), ammonium chloride (ACS reagent, > 99.5%, Sigma-Aldrich).

**Synthesis of bulk 2H MoS<sub>2</sub>.** Firstly, 1.00 g (4.13 mmol) of Sodium molybdate was mixed with 90 mL of DI water in a 200 mL beaker. Next, 0.93 g (12.39 mmol) Thioacetamide (TAA) was added to that beaker and stirred for 15 min. Then, the well-mixed solution was transferred into a 120 mL Teflon-lined stainless-steel autoclave, which was then kept at 180 °C for 24 h in a vacuum oven. After that, the autoclave was naturally cooled down to room temperature, and some black-coloured precipitates can be obtained after washing the residual product inside the autoclave. The washing process includes deionized water (×2) and absolute ethanol (×1) by centrifugation at 15,000 rpm for 5 minutes. Finally, the obtained products were dried in a vacuum oven (60 °C, overnight) and annealed at 700 °C for 4 h under 95% N<sub>2</sub> + 5% H<sub>2</sub> atmosphere.<sup>1</sup>

**Synthesis of 2H/1T MoS<sub>2</sub> powder (UV/NH<sub>4</sub>Cl system).** 20 mg bulk 2H MoS<sub>2</sub> powders were exfoliated in a 10 mL N, N-dimethylformamide (DMF) by using a tip sonication (100 W; Converter Model CV33 UP 100; Cromtech) for 180 min. Then, the mixture was centrifuged at 1,000 rpm to remove large unexfoliated pieces. After that, a certain amount of ammonium

chloride with the weight ratio of MoS<sub>2</sub>: NH<sub>4</sub>Cl = 1: 10 was added to the collected supernatant and mixed in a quartz beaker. The use of quartz beaker aimed to minimize the adsorption of UV light by glassware. The mixture was then exposed to UV light for 18h with a wavelength of 254 nm (UVC, 55 W, Philips, TUV PL-L 55W/4P) in an enclosed box under continuous stirring. The whole solution was then washed with deionized water three times by centrifugation at 8,000 rpm for 15min to remove the residual ammonium chloride. Finally, the collected black powders (UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub>) were dried in a vacuum oven at 60 °C for 24 h.

### **Material Characterization**

Ultraviolet-visible spectroscopy:

The optical properties of synthesized MoS<sub>2</sub> were evaluated by UV-vis spectroscopy (LAMBDA 365 UV/Vis Spectrophotometer). The spectrum for as-prepared bulk MoS<sub>2</sub> and UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub> suspensions were recorded within the wavelength from 400 to 800 nm.

X-ray diffraction:

The differences in interlayer spacing between as-prepared bulk MoS<sub>2</sub> and UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub> powders were examined by X-ray diffraction (XRD) analysis using a Bruker D8 Advance Diffractometer with a Cu ( $\lambda = 1.54 \text{ \AA}$ ) X-ray radiation. The XRD patterns were collected at a scan rate of 0.1°/min and a step size of 0.04° from 5 to 75 degrees.

Raman spectroscopy:

Raman study, in this case, was performed using a Renishaw Invia Visible micro-Raman spectroscopy. The measurements were taken under 514 nm laser excitation and the wavenumber range was from 100 to 500 nm<sup>-1</sup>. The Raman spectra of as-prepared bulk MoS<sub>2</sub> and UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub> samples were recorded by depositing the powders on the clean glass substrates. To verify the stability of the UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub> samples, these powders were exposed to air for 120 days or one year and then deposited on glass substrate again for Raman studies.

Sheet resistance measurement:

To prepare the samples for sheet resistance measurement, MoS<sub>2</sub> powders before and after UV/NH<sub>4</sub>Cl treatment were dissolved in DI water and sonicated by tip sonication for 5 min to

make a suspension. Then, the suspensions were vacuum filtrated on alumina supports to make membranes and dried naturally. After that, the sheet resistance measurements were taken in these membranes via four-point probe measurements (KSR4, Everbeing probe station).

Scanning electron microscopy:

Scanning electron microscopy (SEM) was used to study the morphology of the MoS<sub>2</sub> after UV/NH<sub>4</sub>Cl treatment. The SEM images were obtained using an FEI Magellan 400 Field Emission Microscope operated at a working voltage and current of 3.0 kV and 6.2 pA, respectively. Energy dispersive X-Ray (EDX) analysis was conducted by a large area SDD x-ray detector equipped with microscopy. The samples were dispersed in water first and then dropped on a silicon substrate.

Transmission electron microscopy:

Transmission electron microscopy (TEM) observations were performed using an FEI Tecnai G2 T20 at an operating voltage of 200 keV. The MoS<sub>2</sub> powders were dispersed in ethanol and then dispensed onto a carbon film supported on a copper grid.

X-ray photoelectron spectroscopy:

X-ray photoelectron spectroscopy (XPS, Thermo Fisher, Nexsa Surface Analysis System) was conducted to study the chemical composition of the synthesized MoS<sub>2</sub> samples. The measurements were taken at a pressure not exceeding  $1 \times 10^{-8}$  mbar equipped with a monochromatic Al-K $\alpha$  X-ray source (spot size 400  $\mu$ m) at a power of 180 W (15 kV  $\times$  12 mA). For each sample, survey scans, Mo 3d, S 2p, and N 1s high-resolution spectra were recorded using an Al K $\alpha$  radiation source. Survey spectra were recorded at a pass energy of 200 eV with a step size of 1 eV. High-resolution spectra were recorded at a pass energy of 50 eV with a step size of 0.1 eV. Thermo Advantage software (Thermo Fisher Scientific, East Grinstead, U.K.) was used in the following data analysis (including peak fitting and identification). For the calibration, all of the binding energies were referenced to the carbon C 1s peak at 284.5 eV.

### **Electrochemical Measurements**

All electrochemical measurements were undertaken in a three-electrode configuration using a *Bio-Logic VSP* electrochemical station. All HER electrocatalytic experiments were conducted using a jacketed cell with the working and auxiliary electrode chambers separated by a low-porosity P4 glass frit. Potentials were measured against either Hg|Hg<sub>2</sub>SO<sub>4</sub>|K<sub>2</sub>SO<sub>4</sub>(sat.)

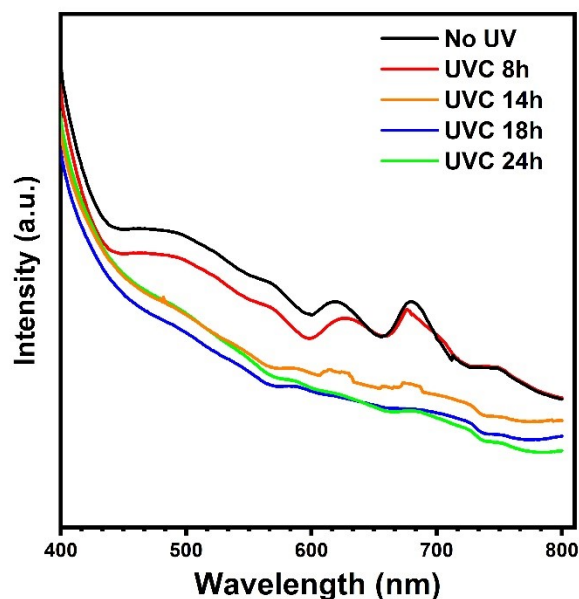
(*Latech*), which were calibrated against a reversible hydrogen electrode (RHE). The reference electrode was confined in a glass capillary positioned at a fixed distance from the working electrode and separated from the working electrode compartment with a P4 glass frit. All measurements utilized a high surface area platinum wire as the auxiliary electrode, which was cleaned using a flame torch between measurements. Following the same techniques, all significant electrocatalytic tests were carried out in 20 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution that was saturated with pure H<sub>2</sub>. A Teflon-lined magnetic stirrer with a 10 mm length, 3 mm diameter, and 500 rpm was always used to agitate the electrolyte solution in order to reduce the effects of mass transport, particularly those related to the development of H<sub>2</sub> bubbles on the electrode surface.

Uncompensated resistance ( $R_u$ ) was calculated from electrochemical impedance spectra (frequency range 200 kHz to 0.1 Hz; amplitude 0.010 V) taken at potentials where no substantial faradaic reactions take place.  $R_u$  levels that were measured fell within a 1–3  $\Omega$  range. Where applicable, the  $IR_u$  product was subtracted to manually post correct the reported potentials for the ohmic losses.

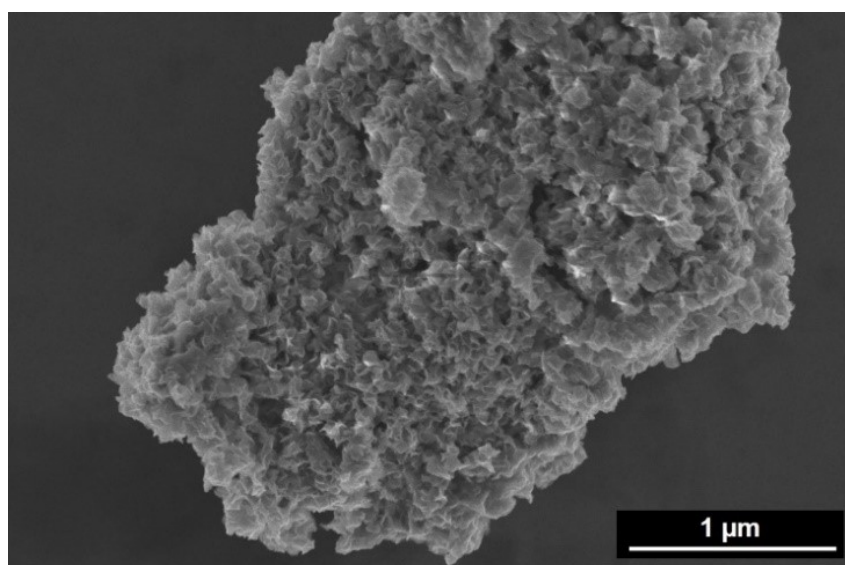
Working electrodes were prepared using carbon fibre paper (*Fuel-cell store*) substrates. CFP electrodes were cleaned by soaking in aqueous 2 M HNO<sub>3</sub> until the formation of gas bubbles was visually observed (usually takes 6 h), washing with water, sonicating in acetone, water, and ethanol for 15 minutes each solvent, and finally drying under an intense N<sub>2</sub> gas flow.

Catalyst (5mg) inks were prepared by dispersing material in 1 mL of a mixture of 0.70 mL water, 0.240 mL isopropanol and 0.050 mL of 5 wt.% Nafion dispersion in ethanol and water by sonication for 30 min (40 Hz, 50 W; Meinhardt Ultrasonics, Germany). In this case, the ultrasound setup equipped with a cooling jacket to avoid heating of the dispersions was used. Freshly dispersed catalyst inks were dropped cast onto clean and dry CFP (loading 0.3 mg cm<sup>-2</sup>) substrates and dried in an oven at 70 °C for overnight prior to testing.

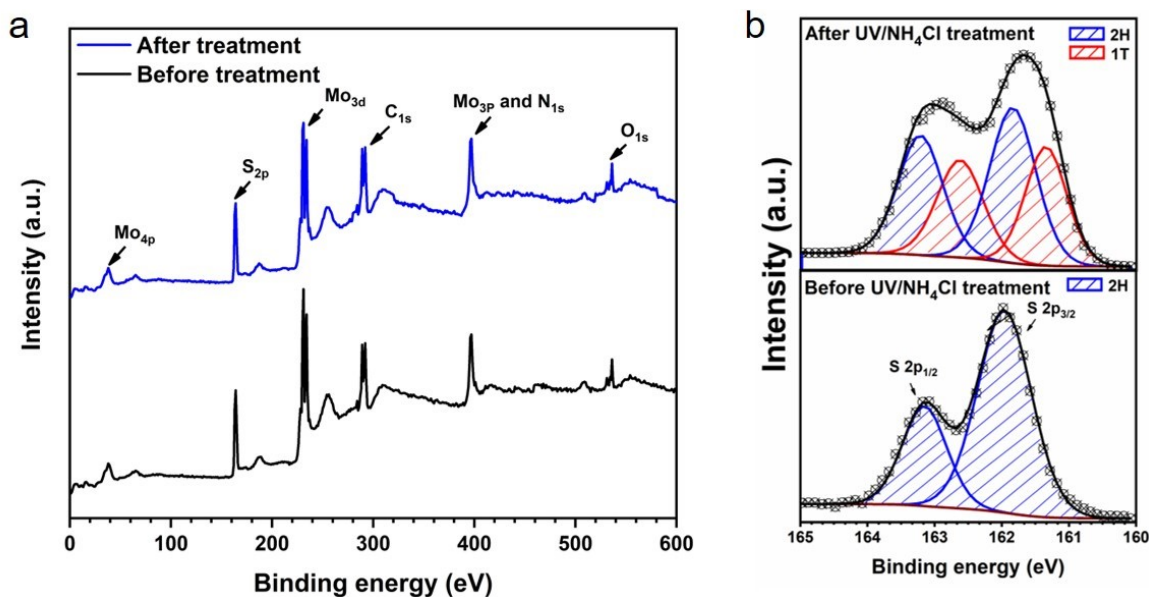
**Additional characterization results for hydrothermally synthesized bulk 2H MoS<sub>2</sub> and UV/NH<sub>4</sub>Cl treated 2H/1T MoS<sub>2</sub> samples.**



**Fig. S1** UV-vis spectra for no UV (as-synthesized 2H MoS<sub>2</sub>), and UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub> (8h, 14h, 18h and 24h) samples. Two adsorption peaks at ~ 618 nm and ~ 679 nm were present in the no UV-treated MoS<sub>2</sub> because of the energy splitting from the valence band spin-orbital coupling. The two adsorption peaks started diminishing with the increase of UV exposure time which can be observed clearly for the 8h and 14h UV-treated samples. The similar UV-vis spectra for UV(+NH<sub>4</sub>Cl) treated for 18h and 24h, indicated that the 1T phase ratio in the collected products did not further increase when the UV irradiation time increased from 18h to 24h.



**Fig. S2** SEM image showing flower-like morphology for hydrothermally synthesized bulk 2H MoS<sub>2</sub> sample.

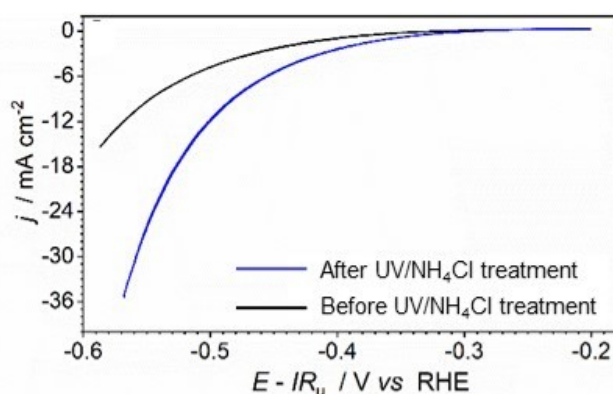


**Fig. S3** (a) XPS survey spectra and (b) High-resolution S 2p XPS spectra for as-synthesized bulk 2H MoS<sub>2</sub> and after UV/NH<sub>4</sub>Cl treated 2H/1T MoS<sub>2</sub> samples.

**Table S1.** XPS high-resolution Mo 3d peak position and FWHM for as-synthesized bulk 2H MoS<sub>2</sub> and after UV/NH<sub>4</sub>Cl treated 2H/1T MoS<sub>2</sub> samples.

	Peak Position		FWHM	
	Before UV/NH <sub>4</sub> Cl treatment	After UV/NH <sub>4</sub> Cl treatment	Before UV/NH <sub>4</sub> Cl treatment	After UV/NH <sub>4</sub> Cl treatment
<b>Mo 2d</b> <sub>3/2</sub>	232.6	232.1	0.8	1.2
<b>Mo 2d</b> <sub>5/2</sub>	229.6	229.0	1.2	1.9

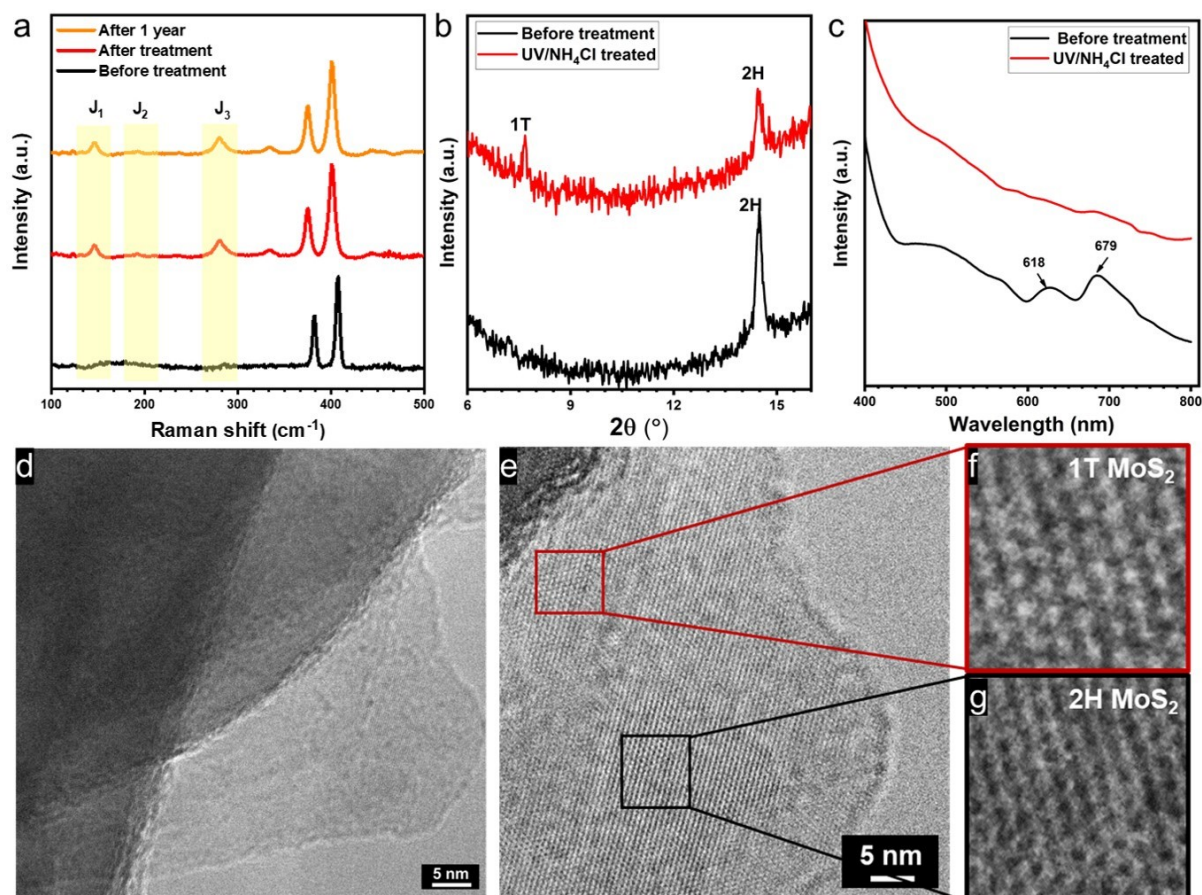
### Electrochemical measurements (HER performance)



**Fig. S4** Quasi-stabilized  $I_{Ru}$ -corrected cyclic voltammetry (scan rate,  $v = 0.005 \text{ V s}^{-1}$ ; 5<sup>th</sup> scans) recorded for as-synthesized bulk 2H MoS<sub>2</sub> (black) and after UV/NH<sub>4</sub>Cl treated 2H/1T MoS<sub>2</sub> (blue) samples immobilized on a carbon fibre paper electrode using a nafion binder in H<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. Currents are normalized to the geometric surface area of the electrode.

### Characterization results for Sigma-Aldrich 2H MoS<sub>2</sub> (after UV/NH<sub>4</sub>Cl treatment)

To explore the universality of the proposed method, we also used the commercial 2H MoS<sub>2</sub> powders (98%; Sigma-Aldrich) as the starting materials. Based on the XRD, Raman, UV-vis and TEM characterization results, 1T/2H mixtures were successfully obtained after the UV/NH<sub>4</sub>Cl treatment.



**Fig. S5** Characterization results for sigma-MoS<sub>2</sub> after UV/NH<sub>4</sub>Cl treatment. (a) Raman spectra (demonstrating 1T phase stability after 1-year of exposure to air) (b) XRD scans (c) UV-vis spectrum for sigma-MoS<sub>2</sub> before and after the UV/NH<sub>4</sub>Cl treatment. (d) Bright-field (e) high-resolution TEM image for UV/NH<sub>4</sub>Cl treated MoS<sub>2</sub>. The generated product is a mixture of 1T and 2H phases, indicated by different morphology in (f) and (g), respectively.



Characterization results for hydrothermal synthesized 2H MoS<sub>2</sub> after UV/NH<sub>4</sub>Cl treatment by a continuous flow set-up

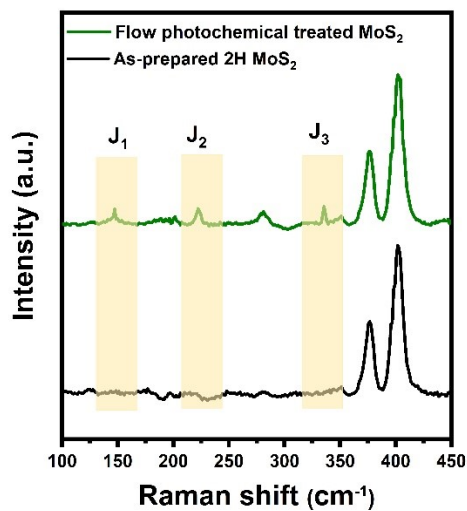


Fig. S6 Raman spectrum for flow photochemical treated MoS<sub>2</sub>.

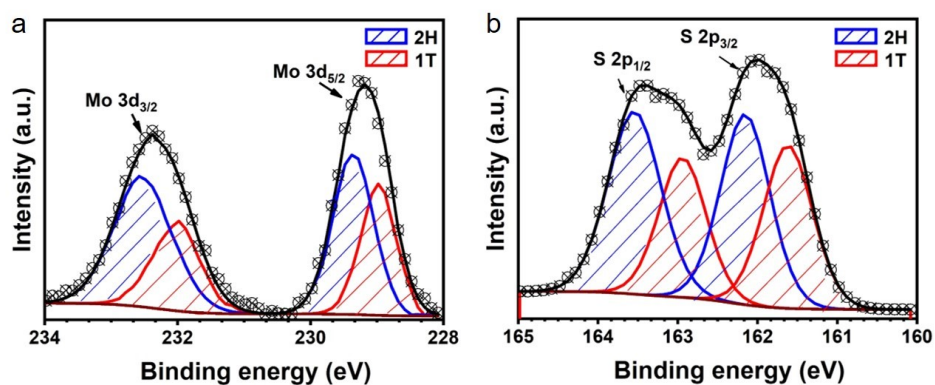


Fig. S7 High-resolution (a) Mo 3d and (b) S 2p XPS spectra for flow photochemical treated MoS<sub>2</sub>. The ratio of 1T phase is estimated at ~ 41%.

Reference

- 1 T. S. Sahu and S. Mitra, *Sci. Rep.* 2015, **5**, 12571.