Supporting Information

Peroxide-Induced Tuning of the Conductivity of Nanometer-Thick MoS_2 Films for Solid State Sensors

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Surface Morphology:

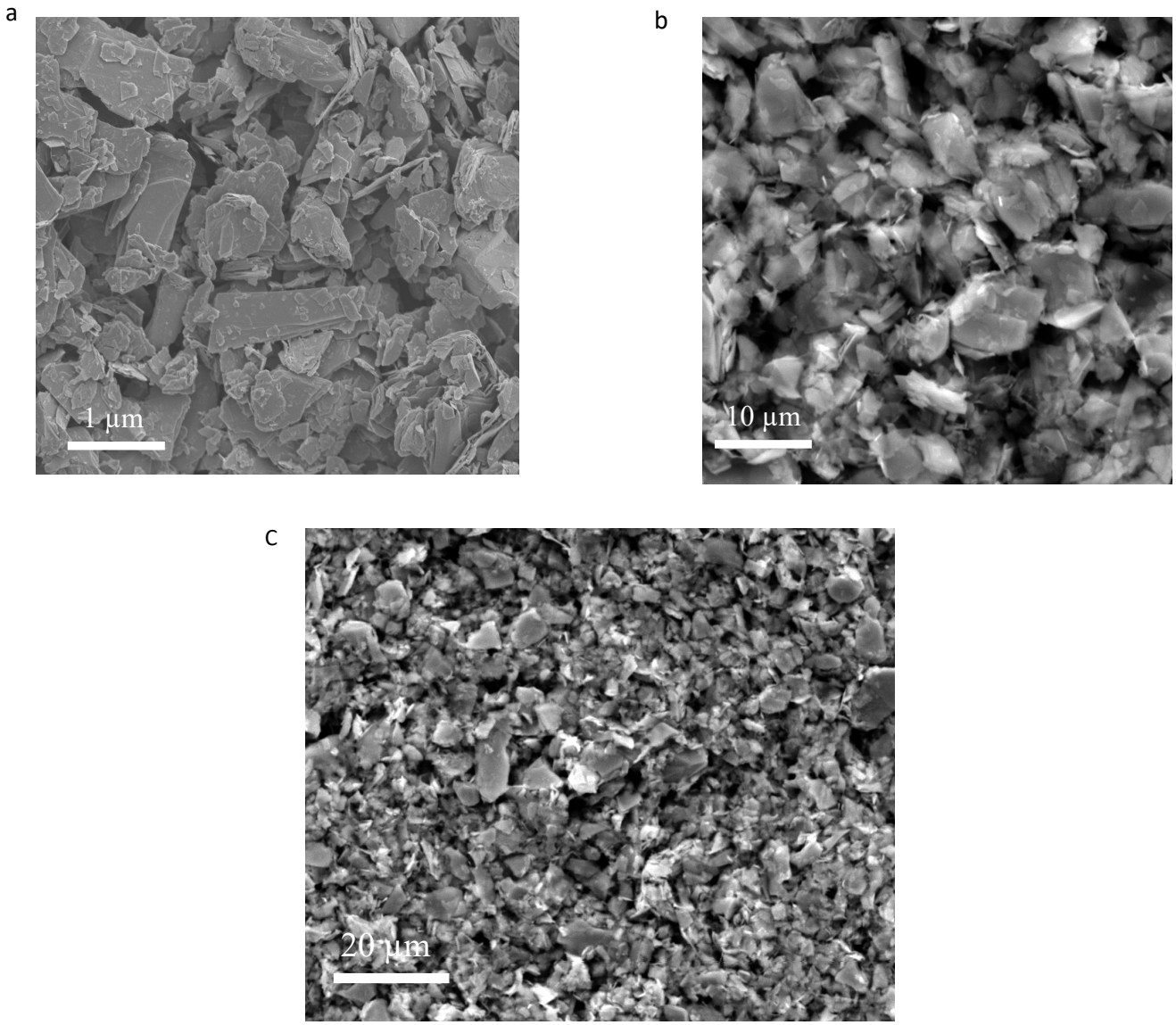


Figure S1: Morphological features of MoS_2 solid films. (a) High resolution SEM image of exfoliated 2H-MoS_2 from bulk MoS_2 powder. Scale bar of the image is 1 µm; (b) and (c) High resolution SEM images of exfoliated c-MoS_2 solid film which obtained from direct sonication of bulk MoS_2 powder in 0.06% H_2O_2. Scale bars of the images are 10 µm and 20 µm, respectively.

Bulk Resistivity Calculation

Sonication Time (minutes)	Sheet Resistance (R_{sheet}) (Ω/□)	Film Thickness (t) (cm)	Bulk Resistivity (ρ) (Ω·cm) [$\rho = R_{sheet} \times t$]
Shaken	2.90E+04	8.49E-04	2.46E+01
2	1.51E+04	8.66E-04	1.31E+01
10	4.00E+03	9.44E-04	3.78E+00
20	4.50E+02	9.35E-04	4.21E-01

Table S1: Bulk resistivity calculation of 0.06% c-MoS_2

Sonication Time (minutes)	Sheet Resistance (R_{sheet}) (Ω/□)	Film Thickness (t) (cm)	Bulk Resistivity (ρ) (Ω·cm) [$\rho = R_{sheet} \times t$]
Shaken	2.10E+04	9.40E-04	1.97E+01
2	1.20E+04	8.90E-04	1.07E+01
10	4.27E+03	9.87E-04	4.21E+00
20	4.36E+02	1.00E-03	4.36E-01

Table S2: Bulk resistivity calculation of 0.06% c-MoS_2 (additional device)

Sonication Time (minutes)	Sheet Resistance (R_{sheet}) (Ω/□)	Film Thickness (t) (cm)	Bulk Resistivity (ρ) (Ω·cm) [$\rho = R_{sheet} \times t$]
Shaken	2.10E+04	1.00E-03	2.10E+01
2	2.23E+04	8.20E-04	1.83E+01
10	4.07E+02	7.60E-04	3.09E-01
20	4.34E+02	9.35E-04	4.06E-01

Table S3: Bulk resistivity calculation of 0.22% c-MoS_2

Sonication Time (minutes)	Sheet Resistance (R_{sheet}) (Ω/□)	Film Thickness (t) (cm)	Bulk Resistivity (ρ) (Ω·cm) [$\rho = R_{sheet} \times t$]
Shaken	2.50E+04	1.47E-03	3.68E+01
2	2.42E+04	9.25E-04	2.24E+01
10	4.00E+02	8.00E-04	3.20E-01
20	4.36E+02	1.00E-03	4.36E-01

Table S4: Bulk resistivity calculation of 0.22% c-MoS_2 (additional device)

Hall Measurement:

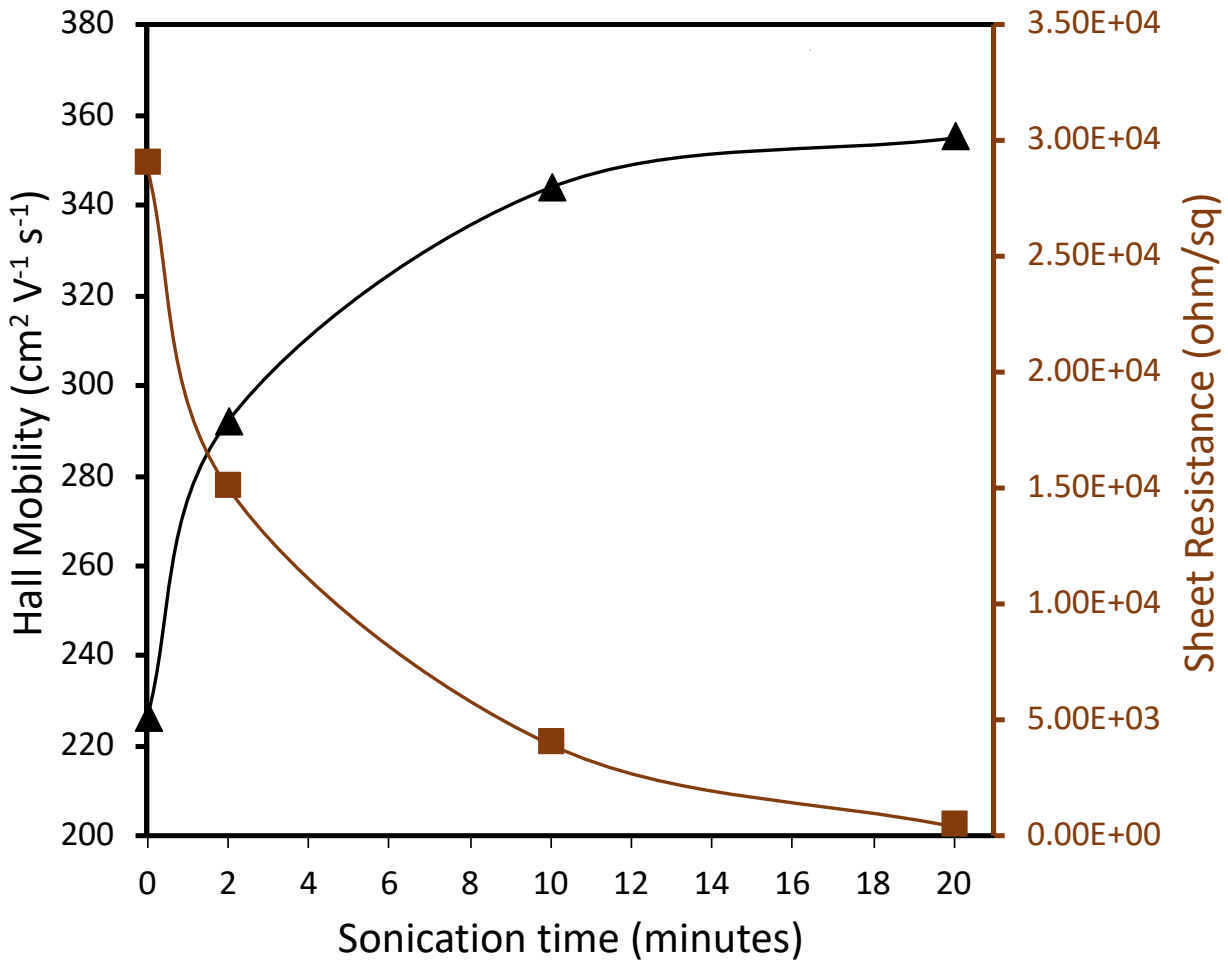


Figure S2: Hall measurements of 0.06% H_2O_2 sonicated samples with different sonication time. The obtained Hall mobility is plotted together with sheet resistance data. The horizontal axis represents sonication time (black colour), primary vertical axis is hall mobility (black colour) and secondary vertical axis (brown colour) is sheet resistance. The highest Hall mobility is obtained at 20 min sonicated sample which has higher conductivity as well.

X-ray diffraction (XRD):

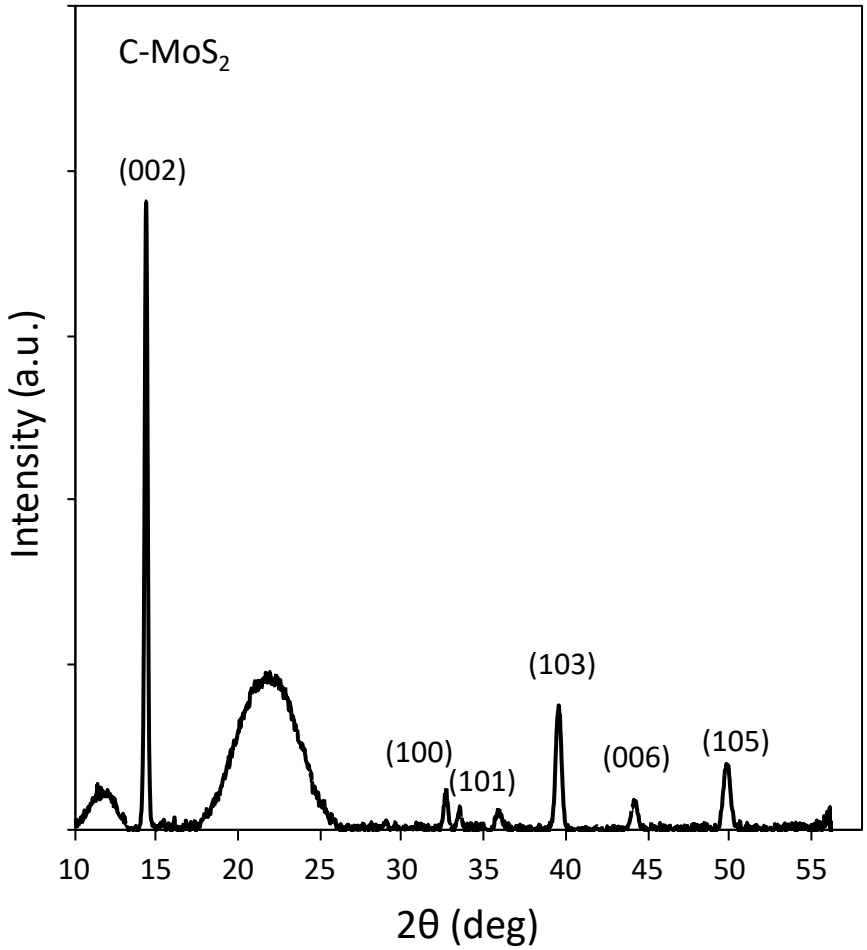


Figure S3: XRD of c-MoS_2 solid film. The two broad amorphous peaks are from the grease (2θ ~12 deg) and glass rod (2θ ~21 deg) used to support the sample. There is no peak for MoO_2 (2θ ~ 25 deg). The rest of the features match well to MoS_2. No other discernible peaks remain unidentified indicating that the crystalline part of the sample was 2H-MoS_2 within the detection limit of the experiment.

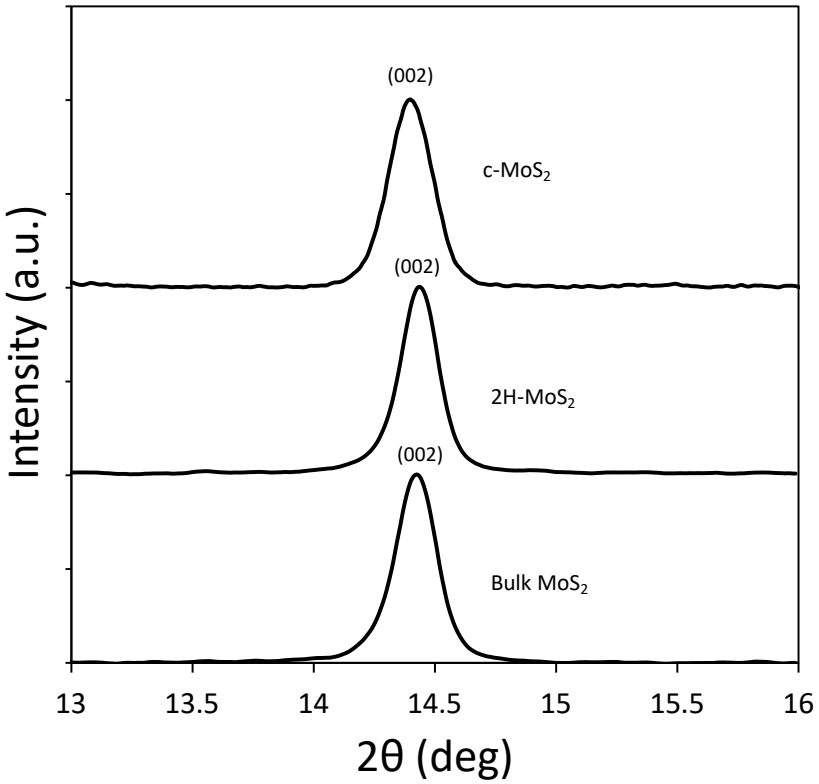


Figure S4: Comparison between the high-resolution XRD (002) peaks near 14.5° of bulk, 2H and conductive MoS_2, showing their crystallographic similarity.

Valance Band of c-MoS_2:

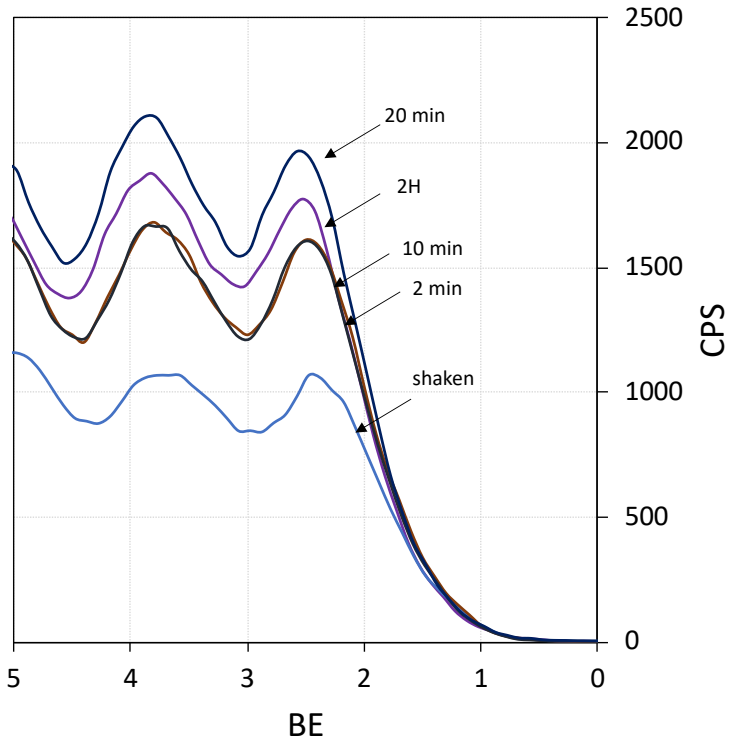


Figure S5: Valance band spectra of 0.06% H_2O_2 c-MoS_2 along with 2H-MoS_2. These spectra are obtained from XPS.

High resolution XPS of 10 minutes sonicated c-MoS_2:

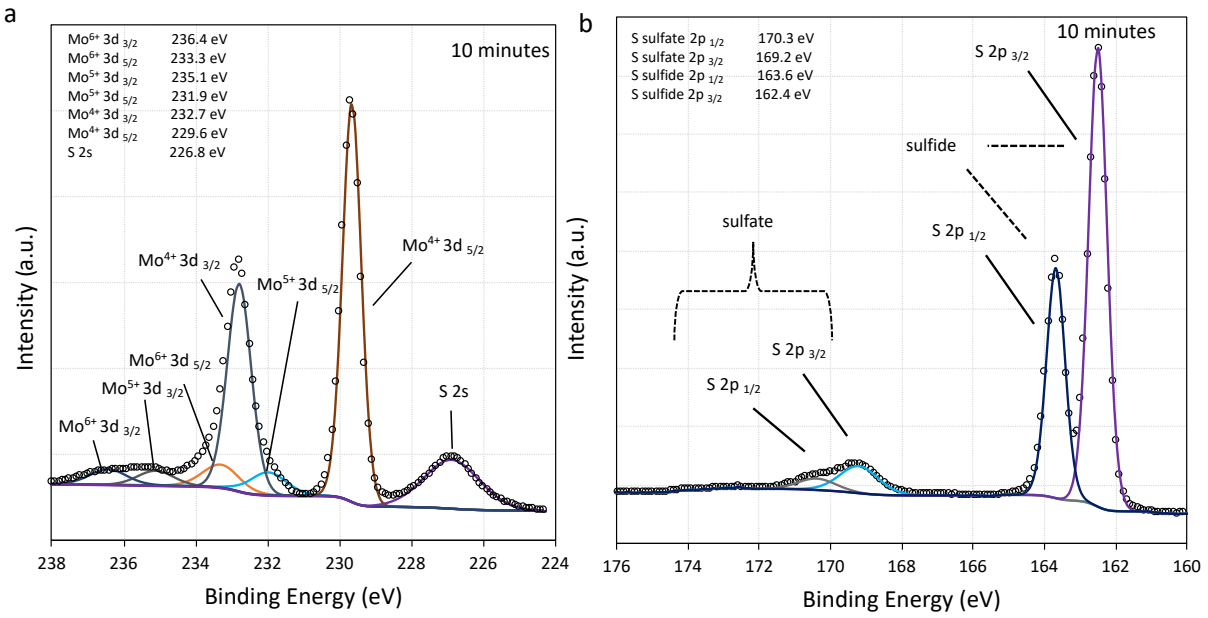


Figure S6: XPS high-resolution spectra of (a) Mo 3d and (b) S 2p peaks of a c-MoS_2 sample sonicated in 0.06% aqueous H_2O_2 for 10 minutes.

High resolution XPS of thiol functionalized c-MoS_2:

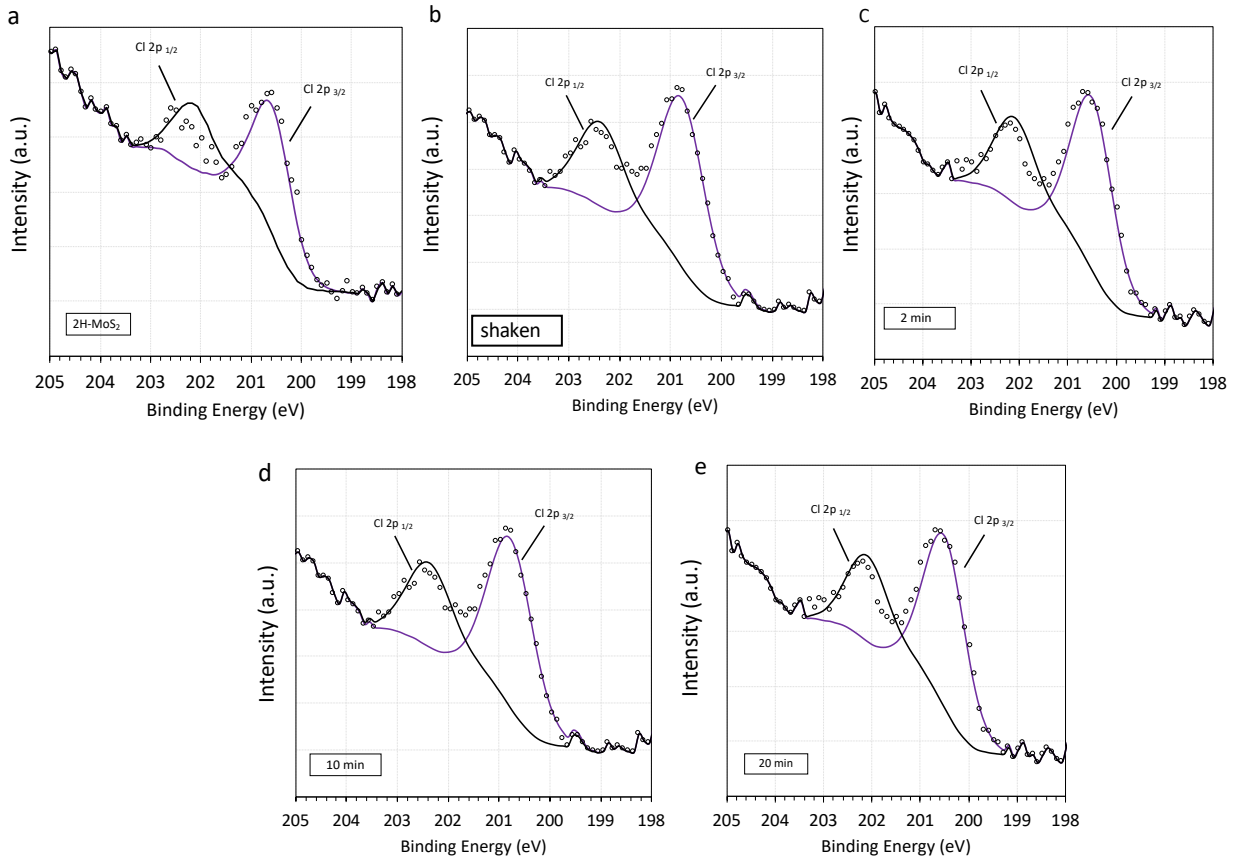


Figure S7: XPS high-resolution spectra of Cl 2p peaks in 4-chlorothiophenol functionalized samples**.** Samples are (a) exfoliated 2H-MoS_2; (b) shaken c-MoS_2; (c) 2 minutes sonicated c-MoS_2; and (d) 10 minutes sonicated c-MoS_2; and (e) 20 minutes sonicated c-MoS_2

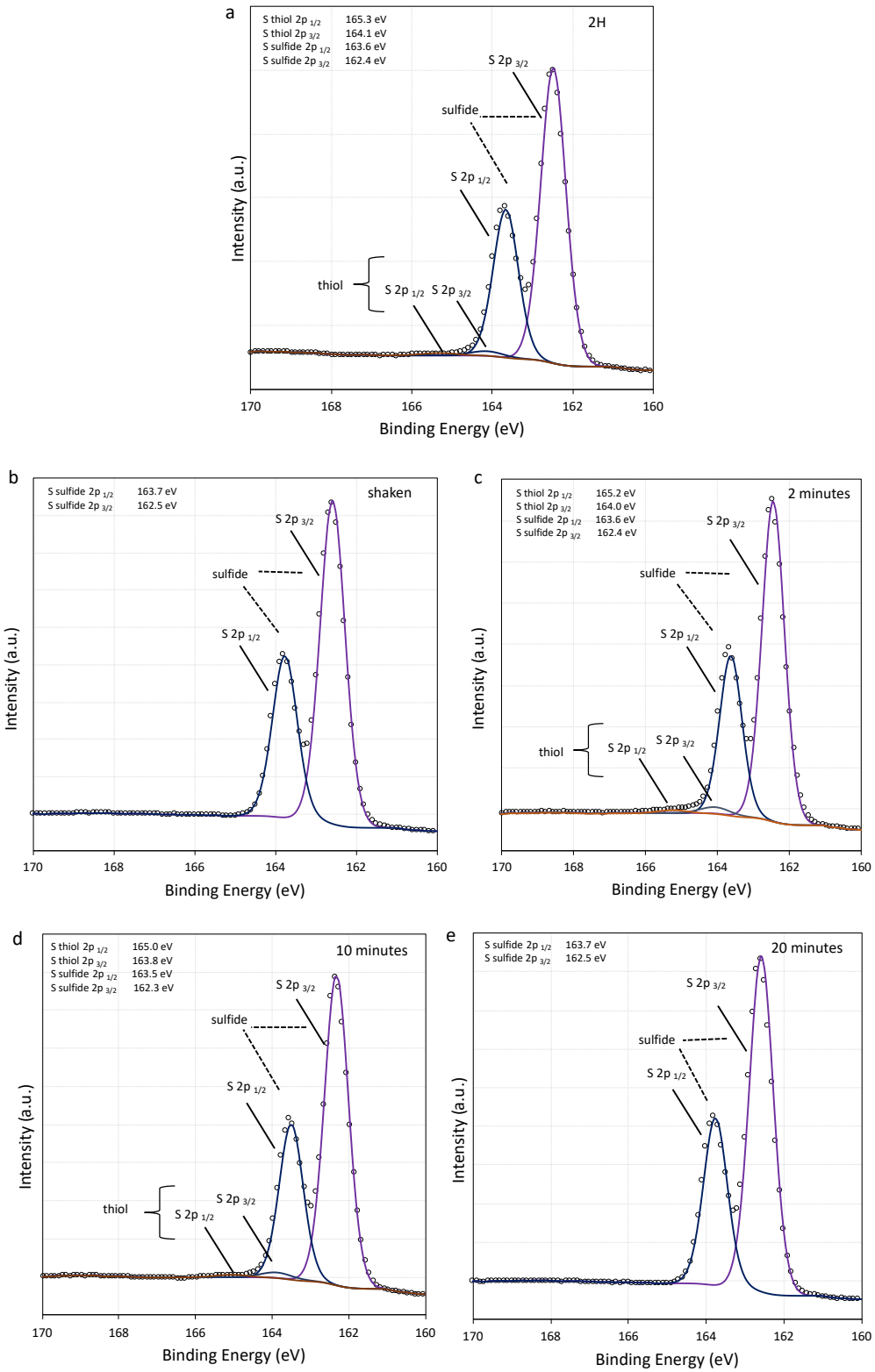


Figure S8: XPS high-resolution spectra of S 2p in 4-chlorothiophenol functionalized samples**.** Samples are (a) exfoliated 2H-MoS_2; (b) shaken c-MoS_2; (c) 2 minutes sonicated c-MoS_2; and (d) 10 minutes sonicated c-MoS_2; and (e) 20 minutes sonicated c-MoS_2

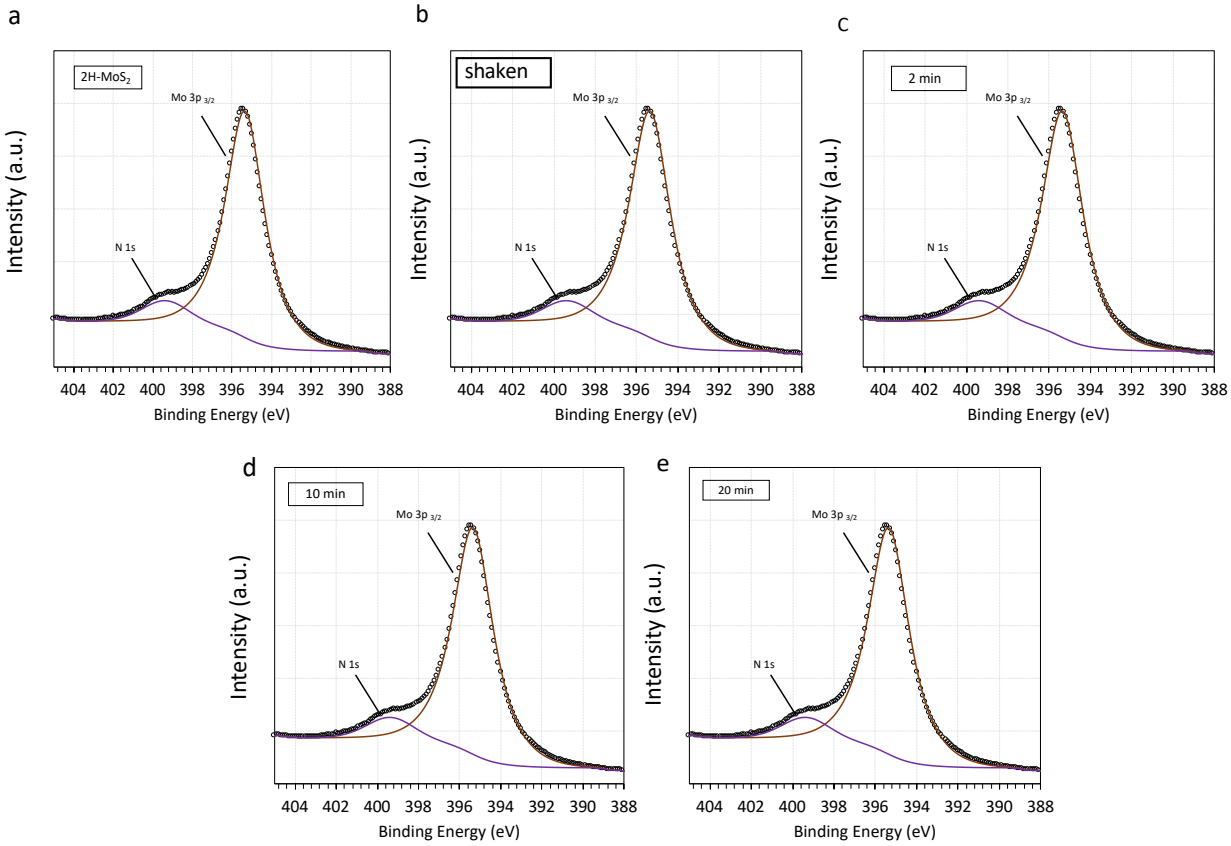


Figure S9: XPS high-resolution spectra of N 1s in cysteamine functionalized samples**.** Samples are (a) exfoliated 2H-MoS_2; (b) shaken c-MoS_2; (c) 2 minutes sonicated c-MoS_2; (d) 10 minutes sonicated c-MoS_2; and (e) 20 minutes sonicated c-MoS_2

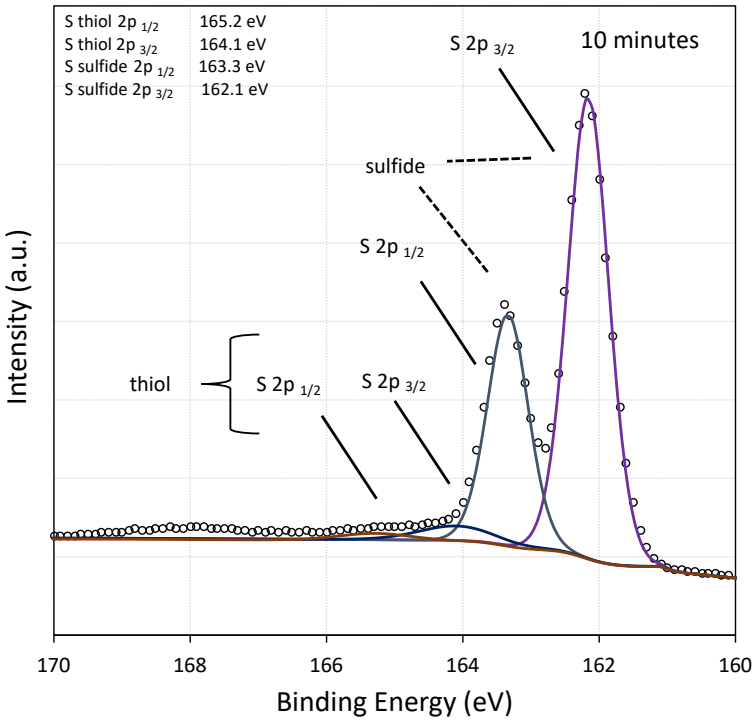
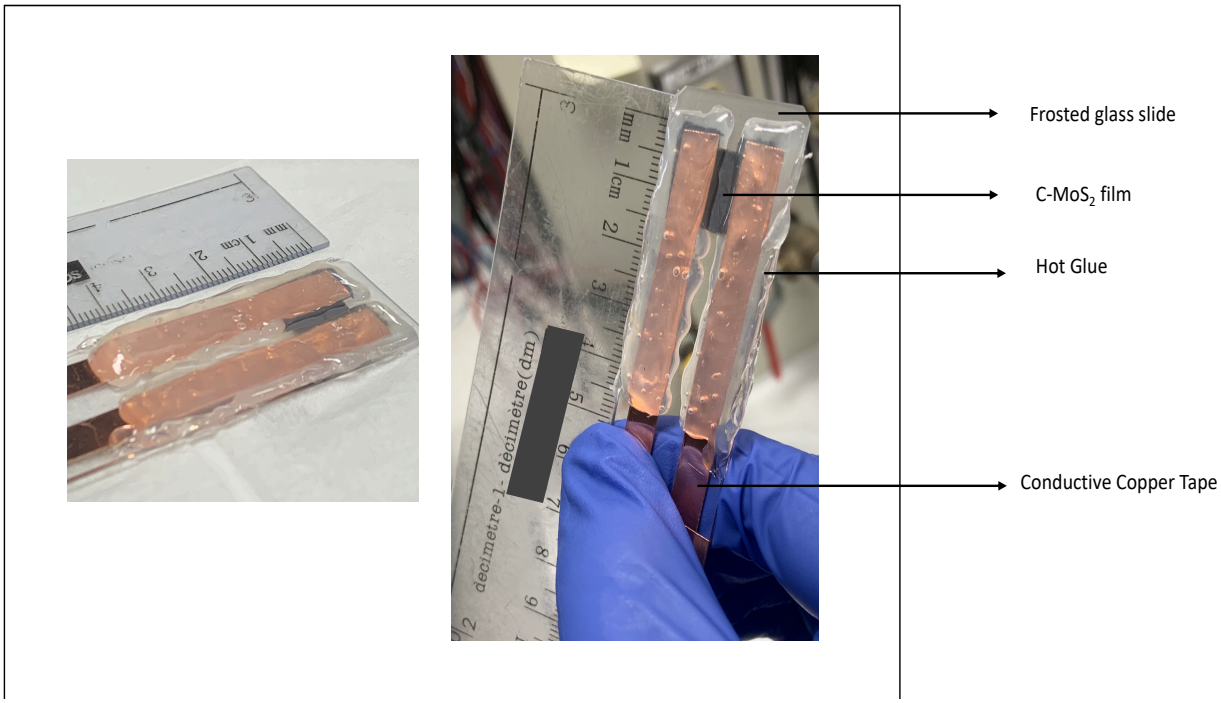


Figure S10: XPS high-resolution spectra of S 2p in cysteamine functionalized 10 minutes c-MoS_2 samples.

Image of chemiresistive c-MoS_2 pH device:



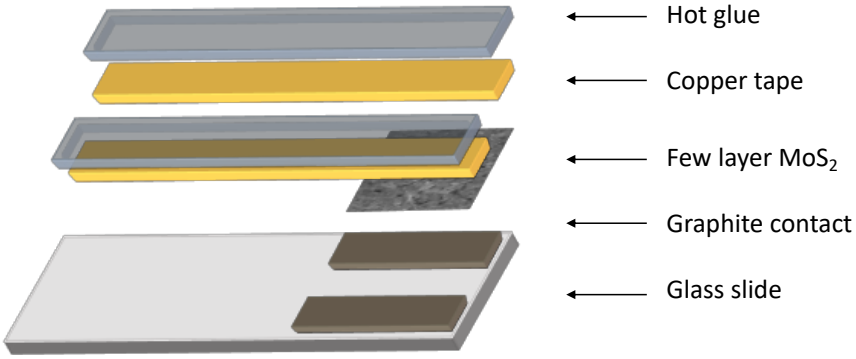


Figure S11: Photographic images of c-MoS_2 chemiresistive devices. A ruler is used to show the dimension of the devices. The dimension of the glass slide is 1" × 3". The dimension of the c-MoS_2 film is ~ 1 cm × 1 cm. Copper foil tape with conductive adhesive (6 mm wide and 0.1 mm thick) is used as metal contacts. Metal contact is covered by hot glue using hot glue gun (Aleene's® ultimate glue gun kit). Schematic representation of the device fabrication steps has also shown below the photographic images.

Conductivity measurements between different fabrication steps:

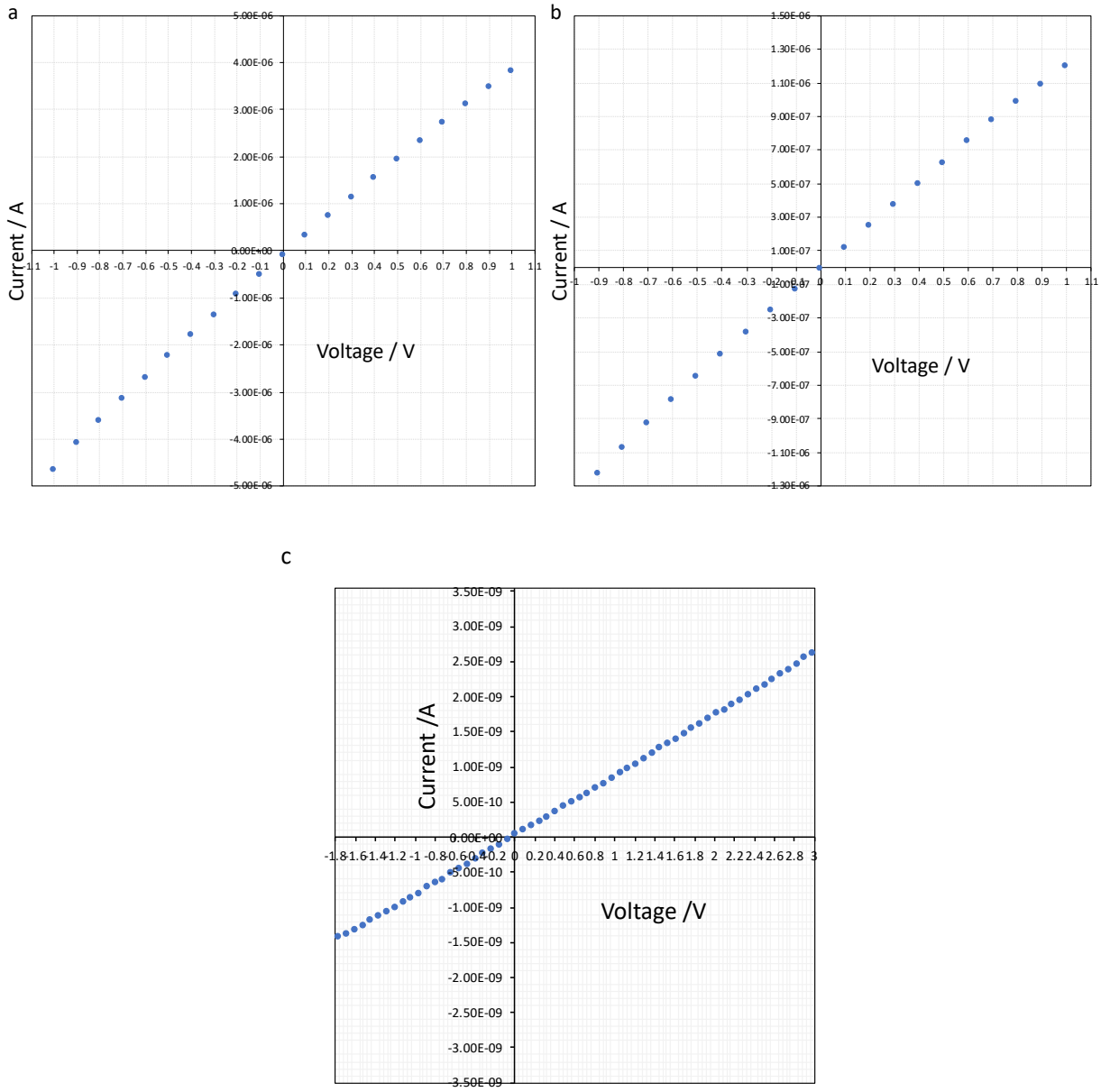


Figure S12: I/V graphs between different stages of fabrication of pristine c-MoS_2 devices. (a) After dropcasting of the c-MoS_2 film; (b) After covering the metal contacts with hot glue. Voltage range was scanned from -1 V to + 1 V (c) after functionalization with cysteamine. Voltage range was scanned from -2 V to + 3 V. Conductivity was measured in air at room temperature before immersing into NaCl solution.

Device response in DI water and NaCl solution:

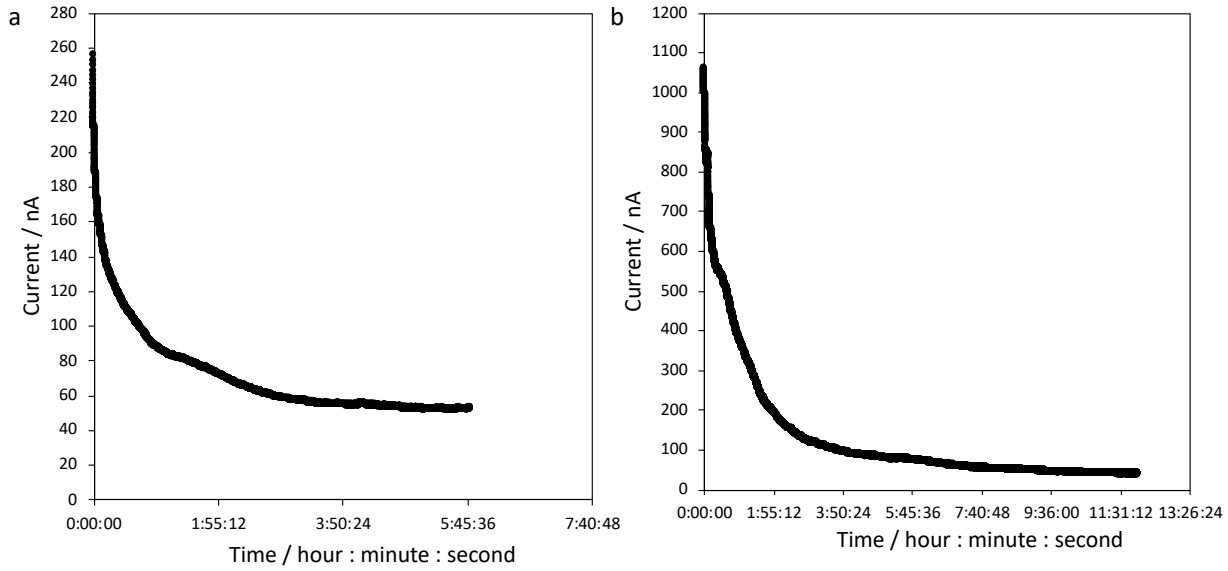
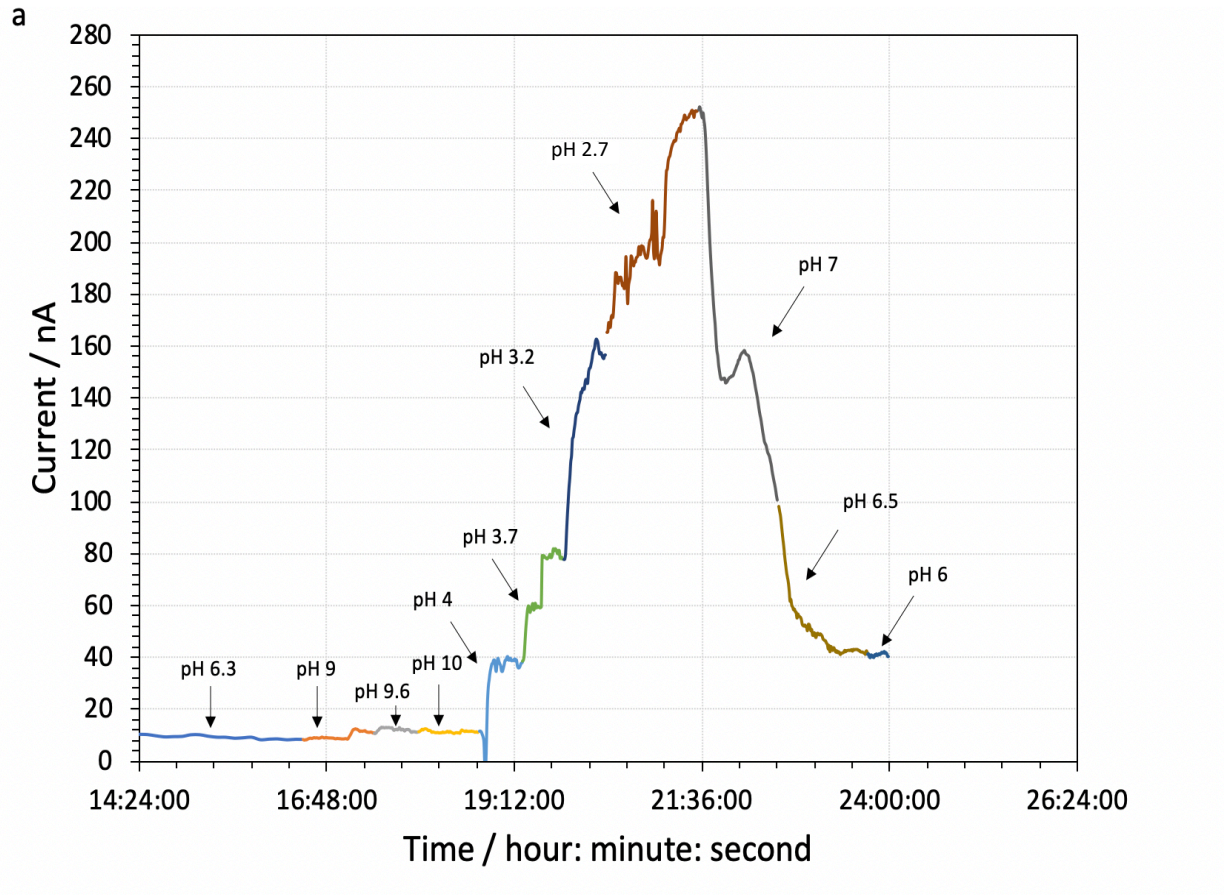


Figure S13: Change in film behavior of pristine c-MoS_2 devices due to transition from air to solution environments before pH measurement. (a) DI water; and (b) NaCl solution. A fixed bias of 80 mV was applied to measure the current changes.

Exploring the full pH range for sensing using cysteamine functionalized c-MoS_2 devices:



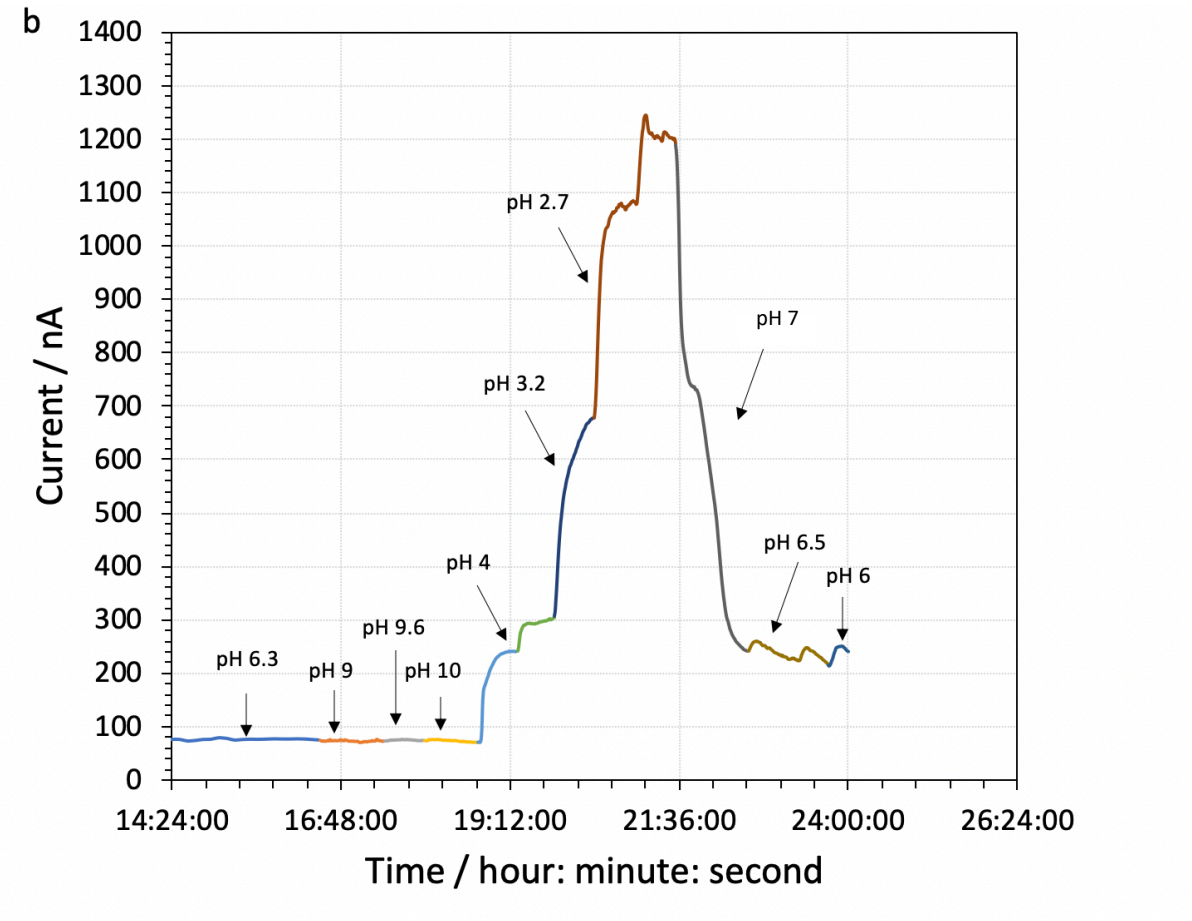


Figure S14: Optimization of pH ranges of two cysteamine soaked c-MoS_2 chemiresistive devices, separately shown in (a) and (b). A fixed bias of 80 mV was applied to measure the current changes. Conductivity changes were not observed from pH 6.3 to 10.

Chemiresistive pH sensing response of pristine c-MoS_2 device:

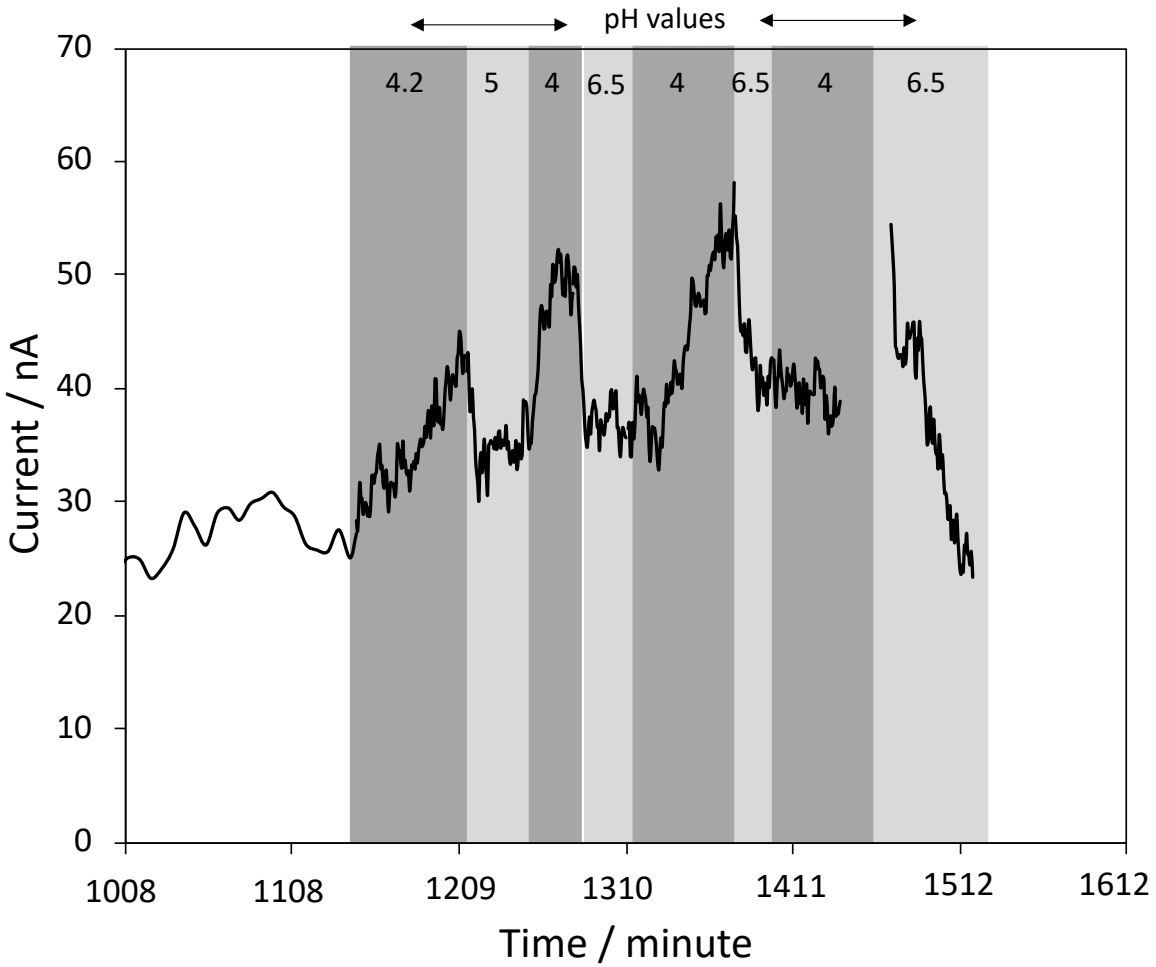


Figure S15: pH sensing response of pristine c-MoS_2 chemiresistive devices. A fixed 80 mV bias was applied to measure the current changes.

Potential *vs.* pH plot:

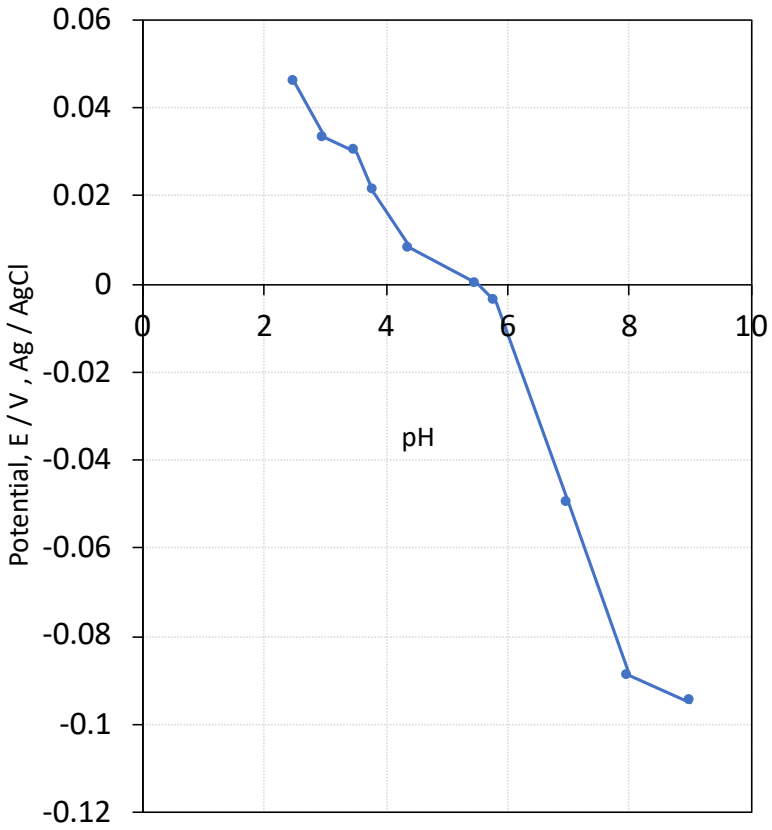


Figure S16: Electrochemical potential (*vs.* Ag/AgCl) of a free-floating c-MoS_2 sensor film as a function of solution pH at room temperature.

Raman Spectroscopy of c-MoS_2 after exposure to pH 2.7:

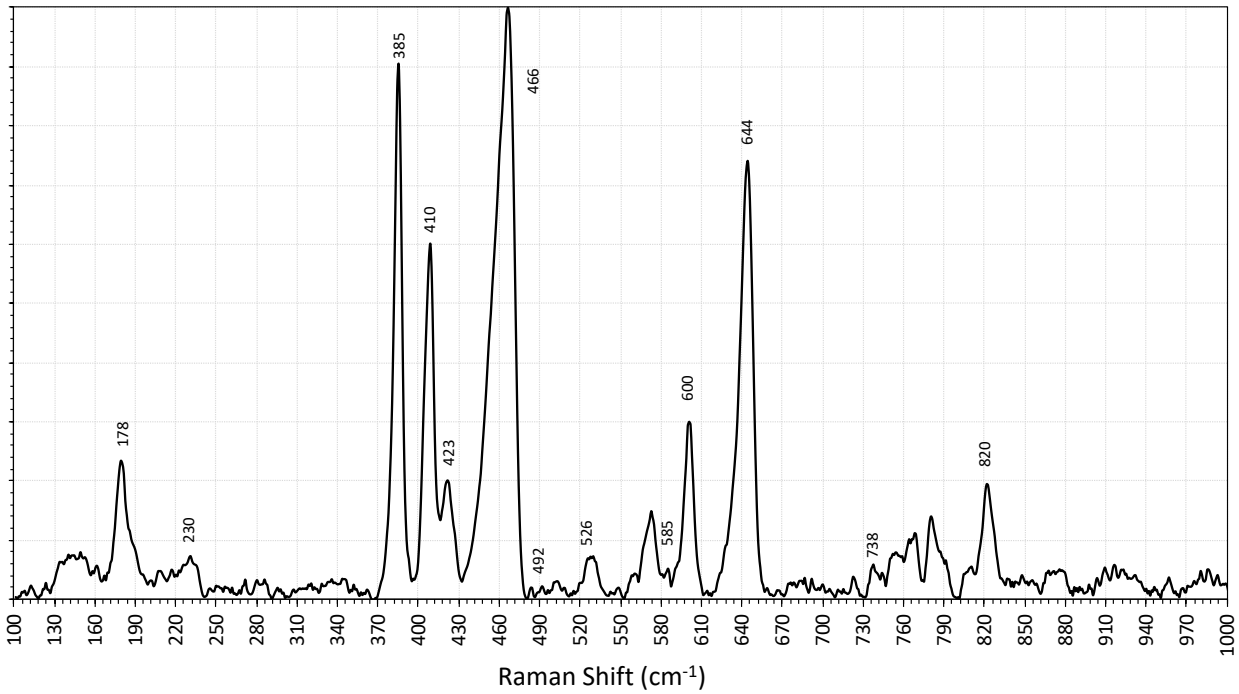


Figure S17: Raman spectrum of c-MoS_2 after exposure to pH 2.7. The sample was illuminated by a 633 nm laser at 1% power. The peak intensity is normalized based on the highest peak of the spectra (~466 cm $^{-1}$). The baseline was corrected using the procedure reported in refs. 1, 2 using Matlab.

Raman Spectroscopy of c-MoS_2 after exposure to pH 9:

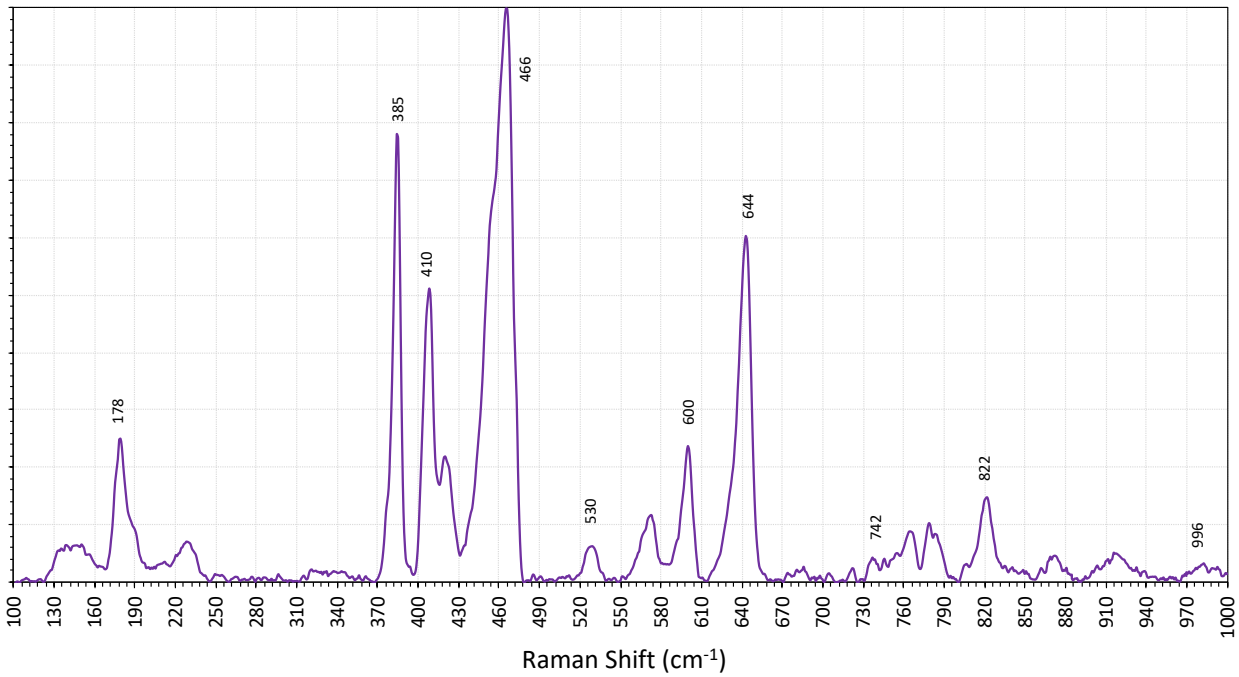


Figure S18: Raman spectrum of c-MoS_2 after exposure pH 9. The sample was illuminated by a 633 nm laser at 1% power. The peak intensity is normalized based on the highest peak of the spectra (~466 cm^{-1}). The baseline was corrected using the procedure reported in refs. 1, 2 using Matlab.

Chemiresistive pH sensing response of undecanethiol functionalized c-MoS_2 device:

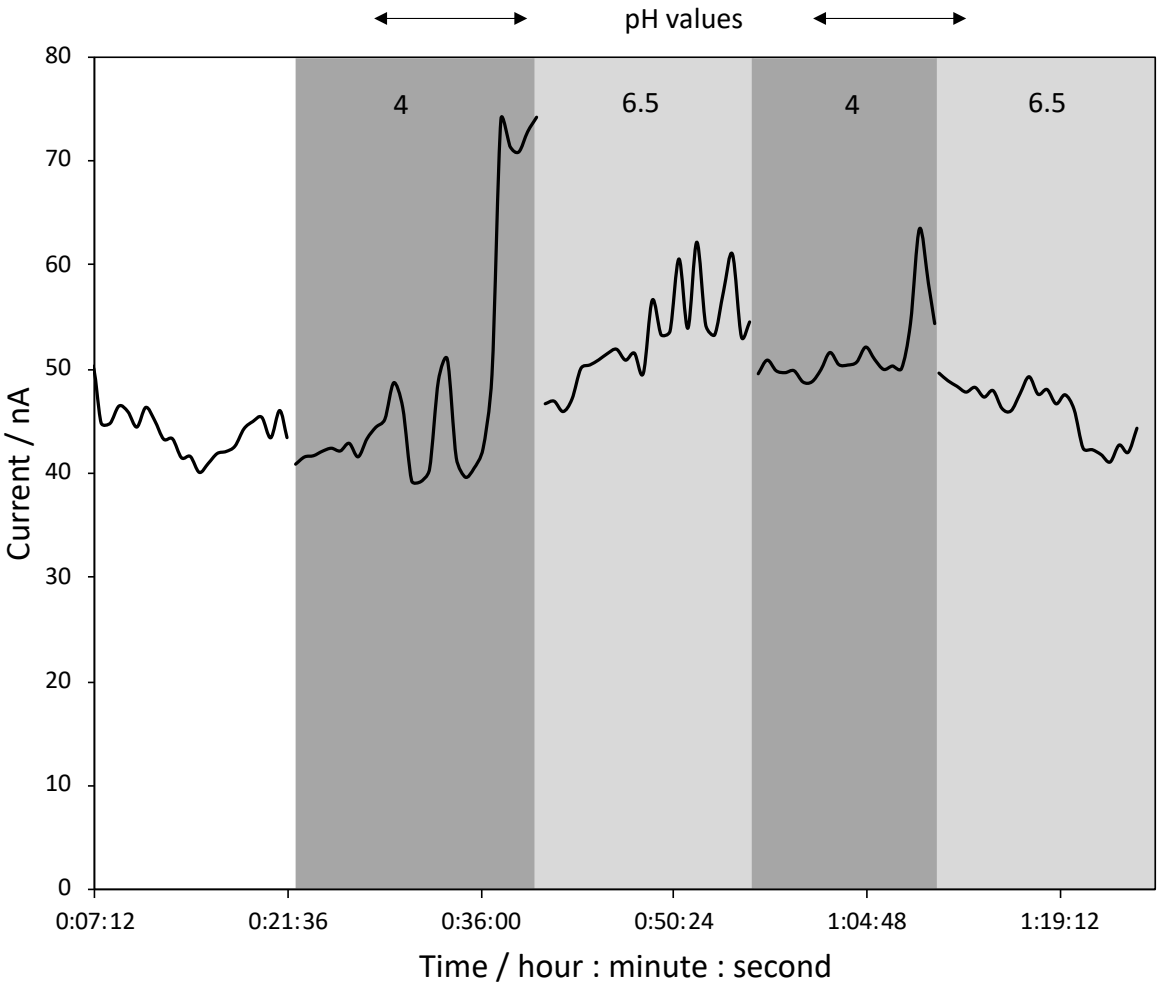
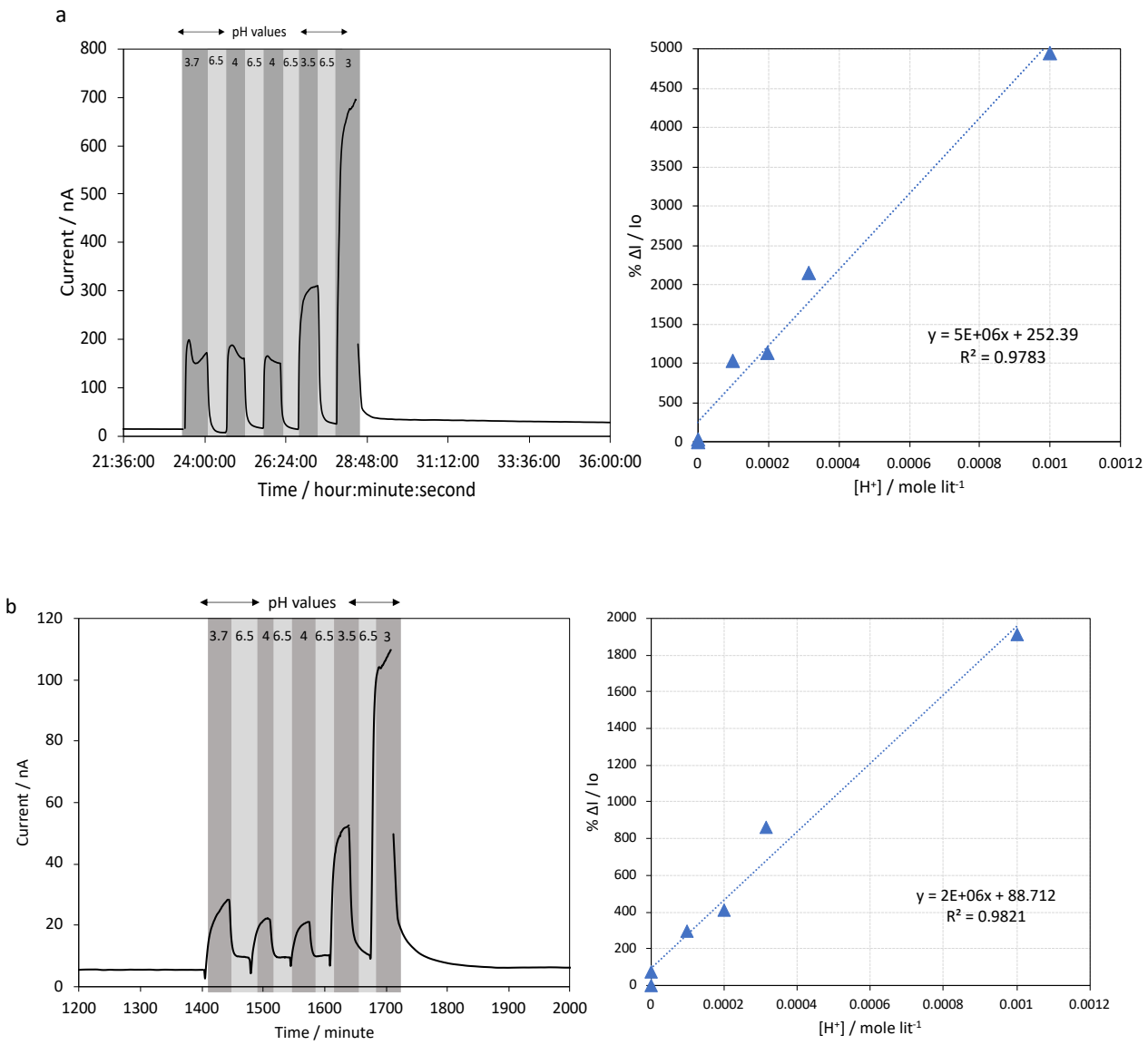


Figure S19: Effect of thiol functionalization on a c-MoS_2 chemiresistive device. Raw data of undecanethiol pH sensing response. A fixed 80 mV bias was applied across the film to measure the current changes.

Chemiresistive pH sensing response of additional cysteamine functionalized c-MoS_2 devices and corresponding calibration curves:



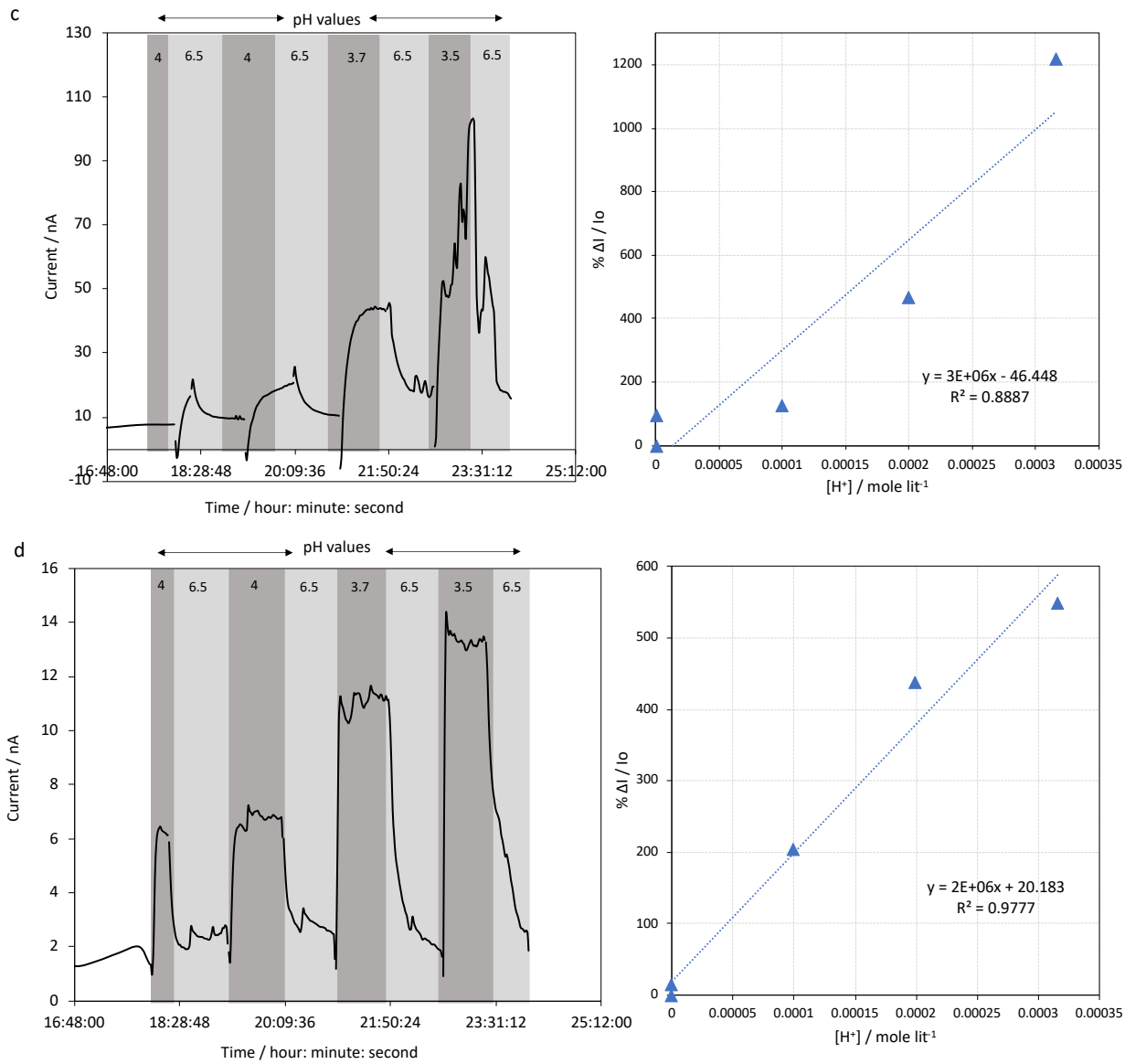
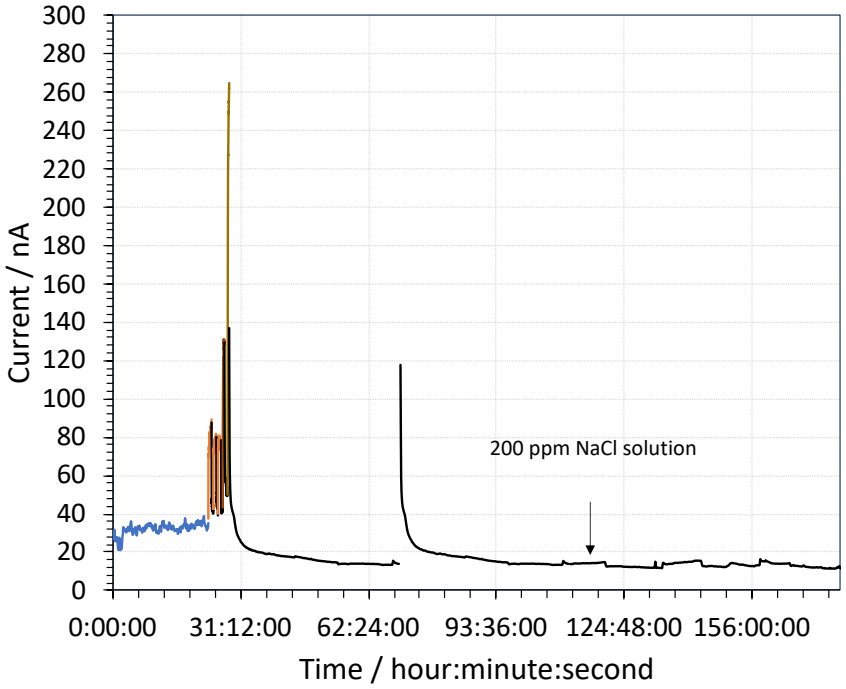


Figure S20: pH sensing response (raw data and calibration curve of sensor response *vs.* pH) of cysteamine soaked c-MoS_2 chemiresistive devices. A fixed 100 mV bias was applied across the film to measure the current changes. (a), (b), (c) and (d) are data for four devices in addition to what is show in Fig. 8, which were run in parallel in order to verify the sensing response reproducibility.

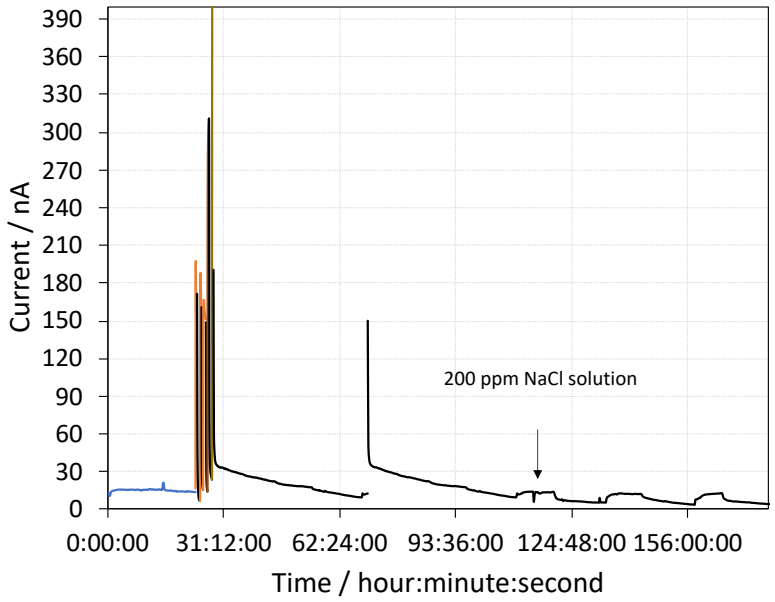
$$Response = \frac{I(actual) - I(background)}{I(background)} \times 100\% \quad \text{(S1)}$$

Long-term stability of cysteamine functionalized c-MoS_2 devices:

a



b



c

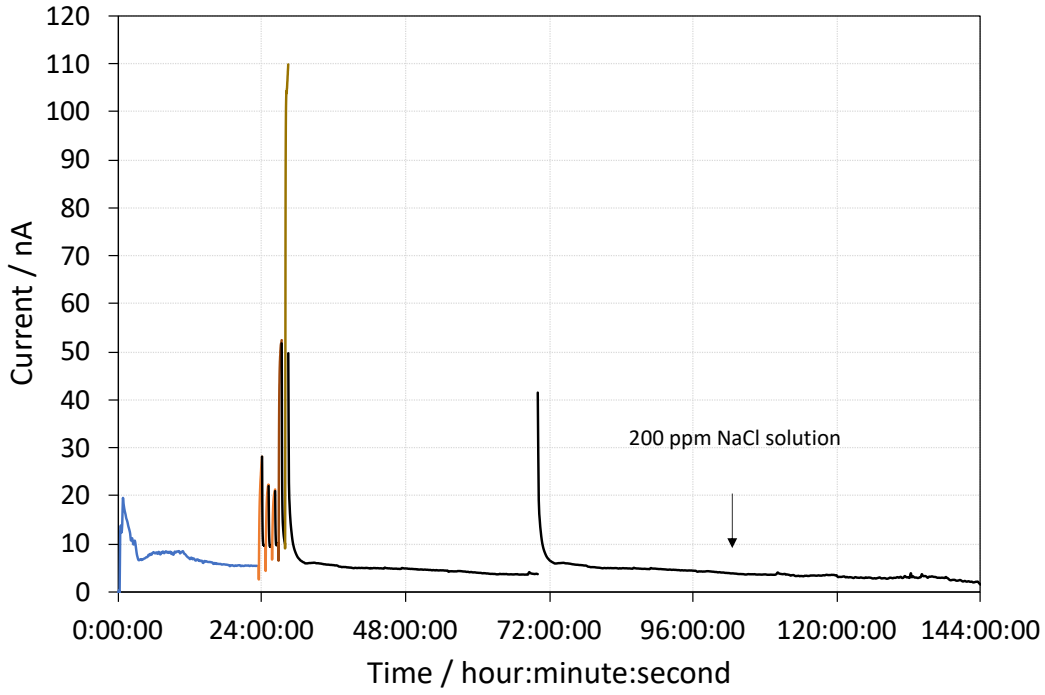


Figure S21: stability of cysteamine soaked c-MoS_2 chemiresistive devices after pH sensing. Solution was replaced with the fresh 200 ppm NaCl solution after pH sensing. A fixed 80 mV bias was applied across the film to measure the current changes. 3 devices were run in parallel to verify reproducibility and long-term stability, with raw data shown for each of the devices in panels (a), (b) and (c). The spikes after 24 hours and after 72 hours are due to pH measurements and replacing the old NaCl solution with fresh NaCl solution.

References:

1. Schulze, H. G.; Foist, R. B.; Okuda, K.; Ivanov, A.; Turner, R. F. B. A Small-Window Moving Average-Based Fully Automated Baseline Estimation Method for Raman Spectra. *Appl. Spectrosc.* **2012**, 66, (7), 757-764.

2. Code developer: Ayad Al-Rumaithi (2020). Raman Spectrum Baseline Removal (https://www.mathworks.com/matlabcentral/fileexchange/69649-raman-spectrum baseline removal), MATLAB Central File Exchange. Retrieved March 16, 2020.