

Supporting Information

Mechanism for Liquid Phase Exfoliation of MoS₂

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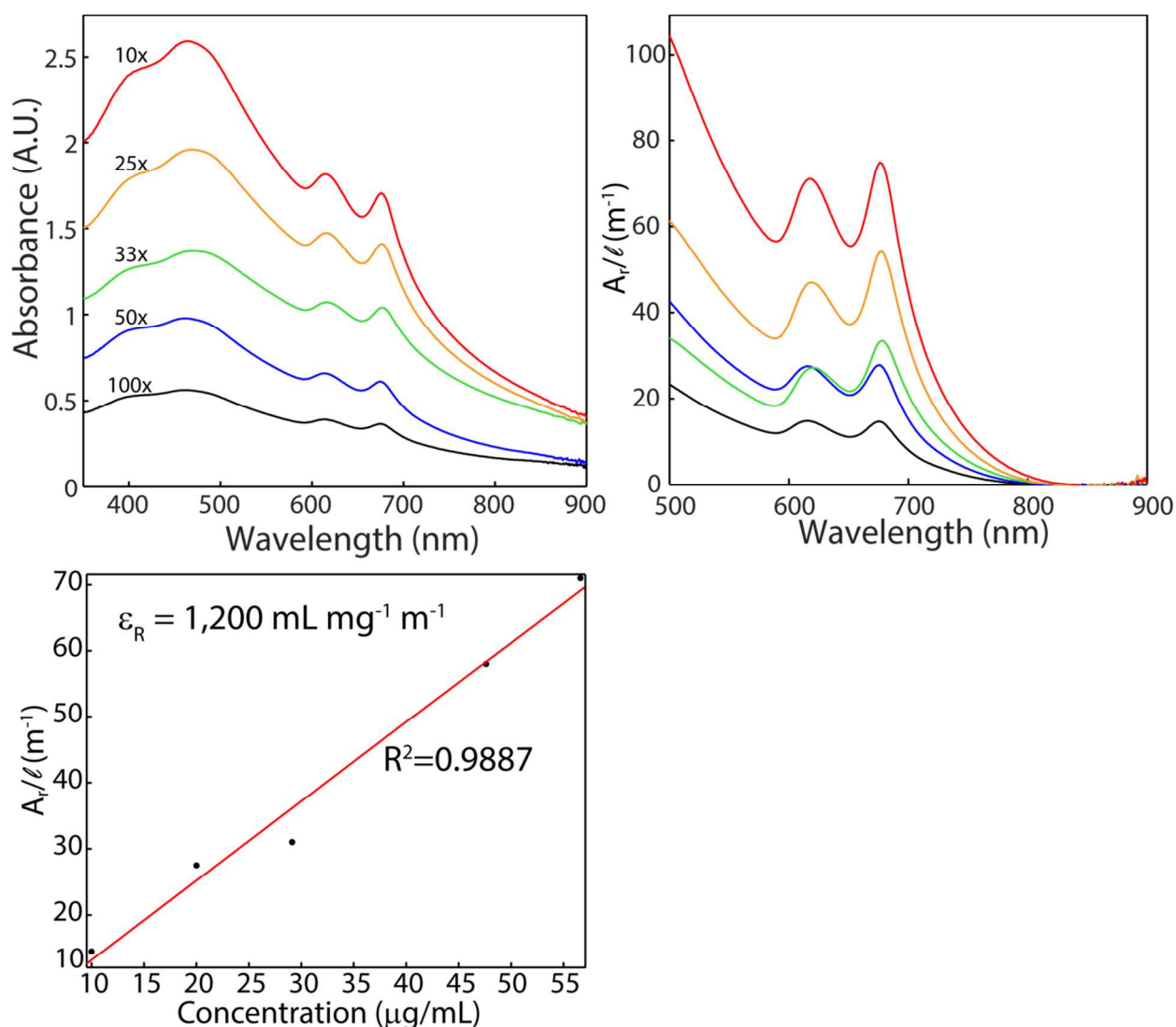


Figure S1. Determination of molar absorptivity. A) Absorption profiles of exfoliated flakes centrifuged at 2,000 RPM (dilution factors indicated). Note the large contribution from scattering at non-resonant wavelengths. B) Absorption profiles after a linear scattering background is subtracted at high wavelength regions. The resonant absorption intensity was extracted from these curves. C) Plotting the resonant absorption against the concentration (determined by mass difference of the parent solution after removal of solvent *via* vacuum distillation) yields the cross-section due to resonant absorption.¹⁻⁴

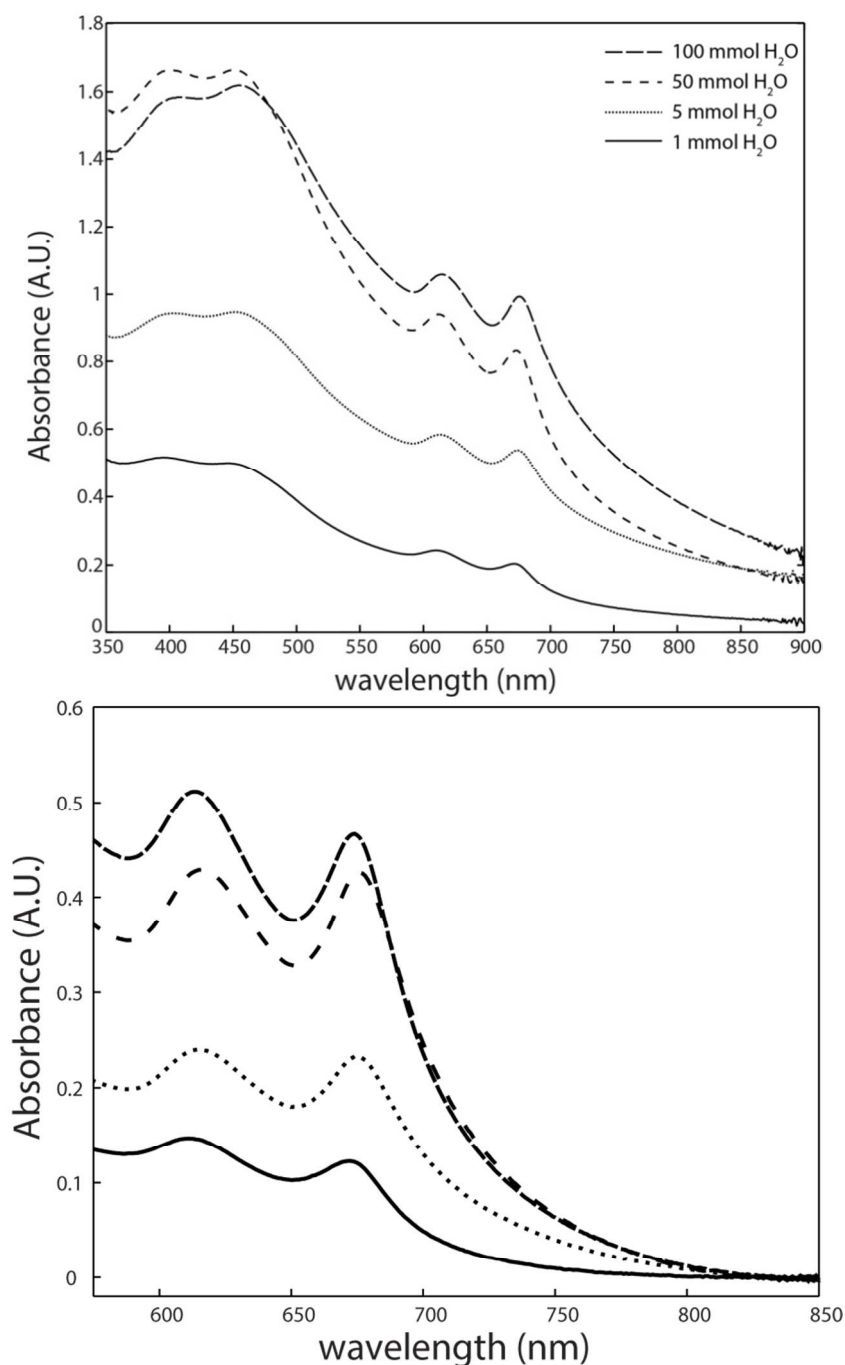


Figure S2. Addition of water to NMP also increases exfoliation yields in flakes isolated at 5,000 RPM. A) Up to a 5-fold increase in yields saturates after 1:1 mol ratio of NMP:H₂O. Note the large scattering background observed for lower centrifugal rates, requiring a scatter correction for accurate representation of concentrations. Thus, the increase in yields is size independent, and similar saturation points are observed between different flake sizes. B) Absorption spectra after background correction.

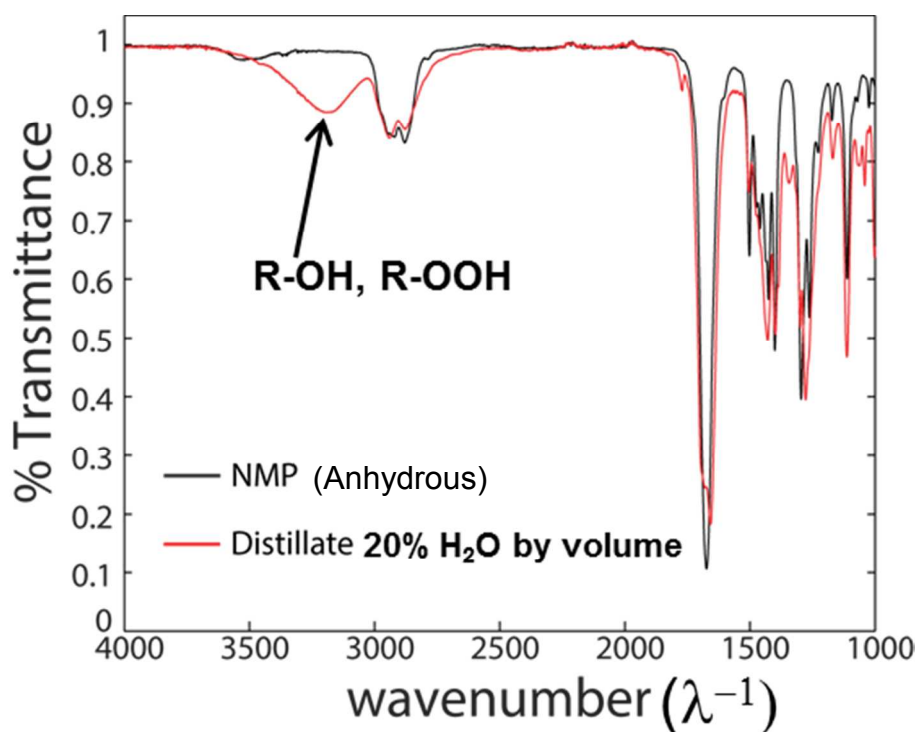


Figure S3. FTIR spectra of anhydrous NMP and distillate. The distilled product show the presence of aliphatic hydroxyl functionalization, while the anhydrous solvent only shows unfunctionalized –OH stretches due to free H₂O in the system (~3500 cm⁻¹). Minimal changes are observed in the carbonyl and amide region, suggesting these functionalities are left undisturbed after oxidation.

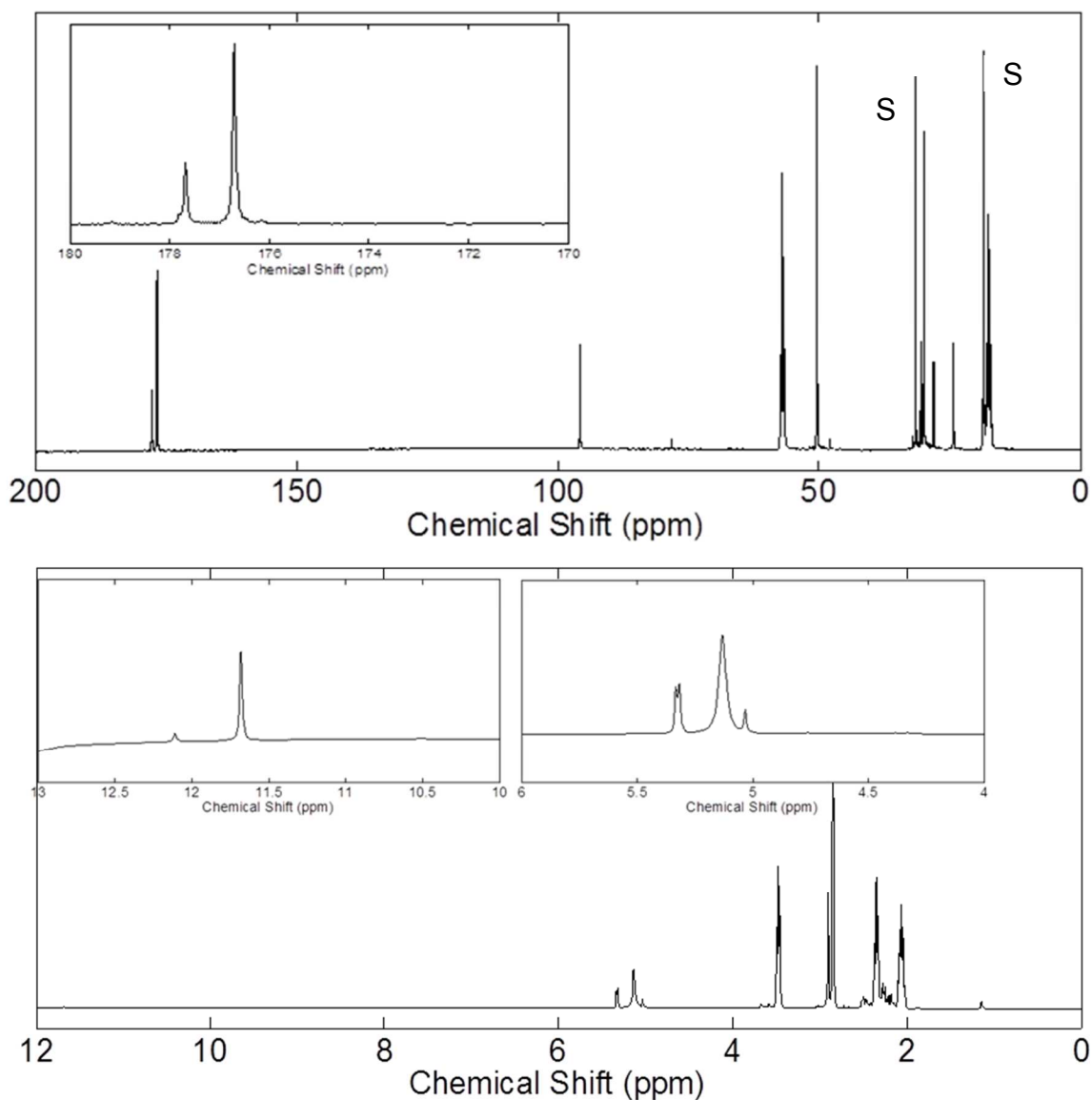


Figure S4. ^1H and ^{13}C NMR of oxidized product after distillation. The spectra show the appearance of secondary amides and carboxylic acids, suggesting a ring opening reaction may be occurring during the oxidation. The carbon peak at 95 ppm may correspond to a γ -peroxide previously reported. Compared to the dry solvent, the emergence of highly deshielded protons may indicate oxidation products.

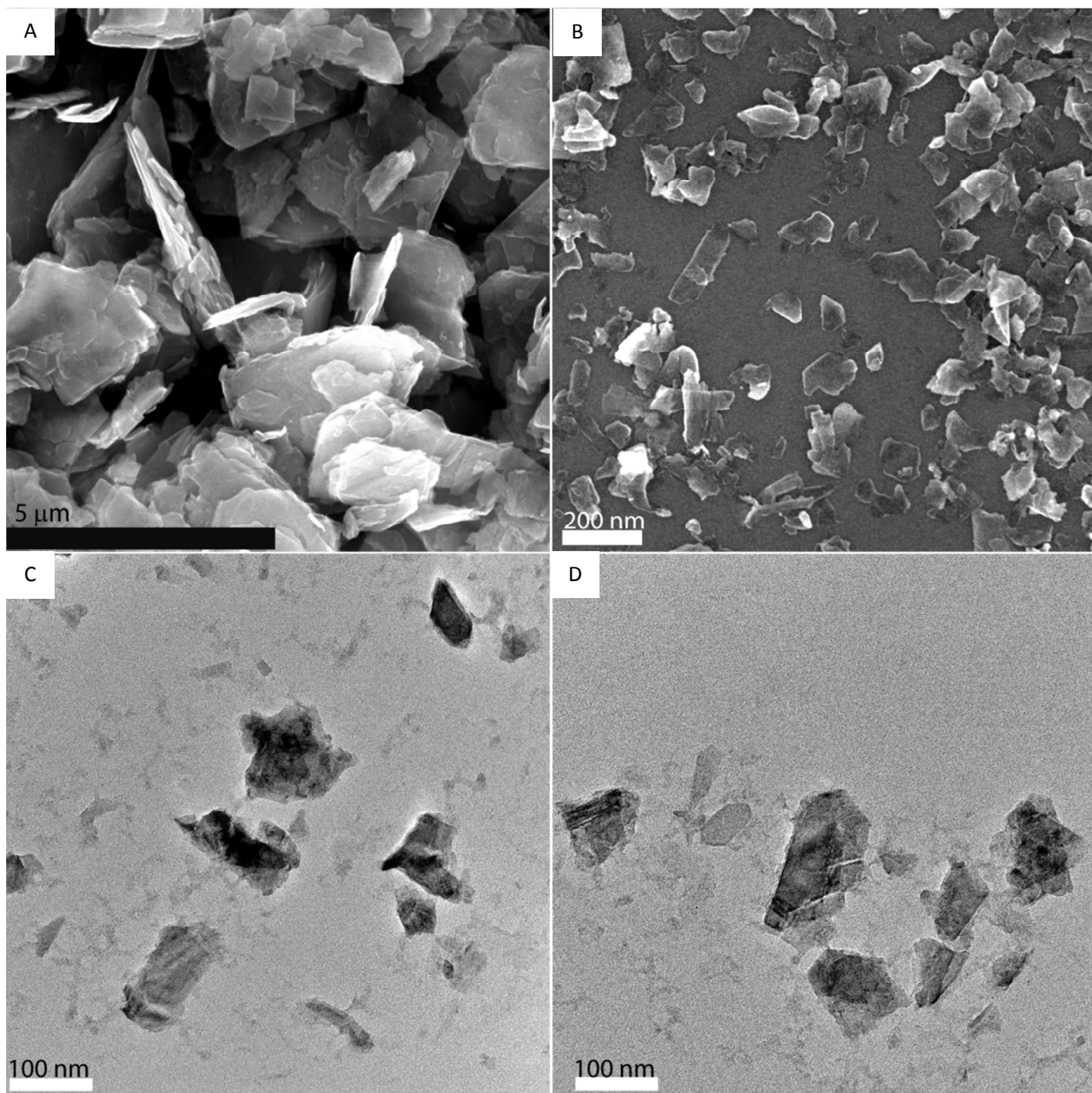


Figure S5. Electron Microscopy of MoS₂. A) Bulk MoS₂ show micron sized layered materials. B) SEM imaged of exfoliated flakes (sonicated 1 hour, centrifuged @ 12.7k RPM) drop-cast on Si wafer showing few- to mono- layered flakes. C,D) TEM of exfoliated flakes (sonicated 1 hour, centrifuged @ 12.7k RPM) illustrating representative morphologies present in exfoliated supernatants.

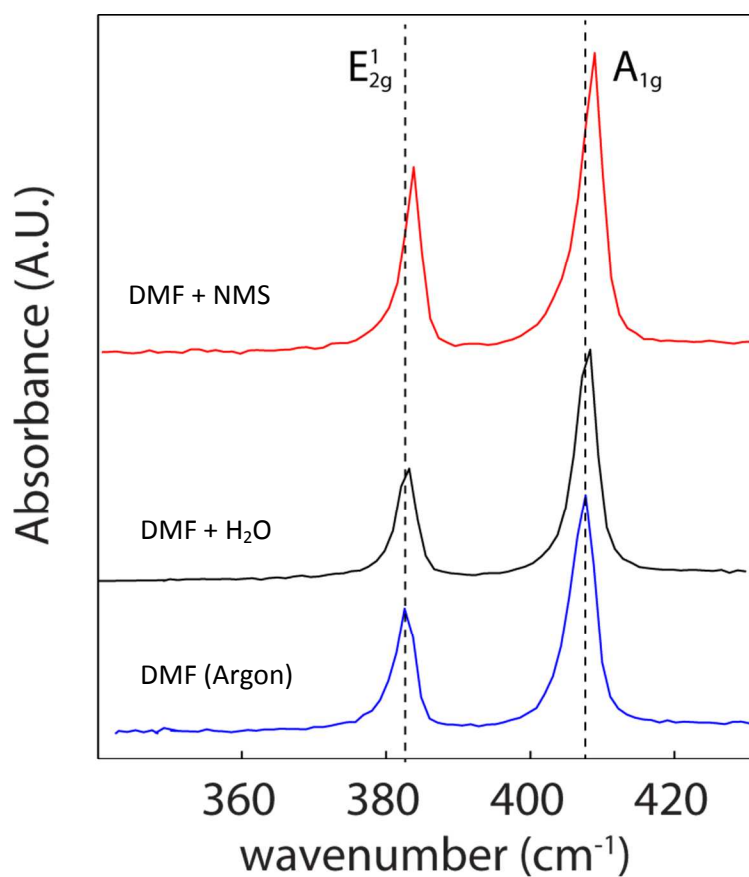


Figure S6. Raman Spectra of dried MoS₂ exfoliated under the indicated conditions. The inclusion of oxidants into the exfoliation mixture seems to have little impact on the position of the peaks. Aside from the observed Raman peaks, no additional peaks were observed. Spectra are off-set for visual clarity.

TS1 Quantitative XPS analysis of exfoliated MoS₂ in the presence of H₂O.

Spin rate (rpm)	Water (mmol)	Mo ⁺⁶ %	Mo ⁺⁴ %	S %	S:Mo	S:Mo ⁺⁴	Mo ⁺⁶ :Mo ⁺⁴
7,000	0	2.5	36.3	61.2	1.58	1.70	0.07
7,000	1	2.7	36.5	60.8	1.55	1.68	0.07
7,000	3	15.5	31.8	52.7	1.11	1.65	0.49
10,000	0	5.7	35.1	59.2	1.45	1.68	0.16
10,000	1	12.6	33.1	54.3	1.19	1.64	0.38
10,000	3	47.9	20.2	31.9	0.47	1.57	2.37
12,700	0	23	29.8	47.2	0.89	1.58	0.77
12,700	1	58.5	19.3	22.2	0.29	1.15	3.03
12,700	3	43.7	22.2	34.1	0.52	1.53	1.97

Table S1. XPS quantification of Mo⁺⁶3d 5/2, Mo⁺⁴ 3d 3/2, and S 2p peaks for samples exfoliated with indicated water content. As the centrifugal speed and water content increases, the extent of conversion from Mo⁺⁴ to Mo⁺⁶ also increases, and the S:Mo ratio also decreases, indicating oxidation and substitution of sulfur for oxygen. Deviations from the expected 2:1 S:Mo for no water added may be due to residual water in NMP or exposure to oxygen during transport from the vacuum chamber to the XPS chamber.

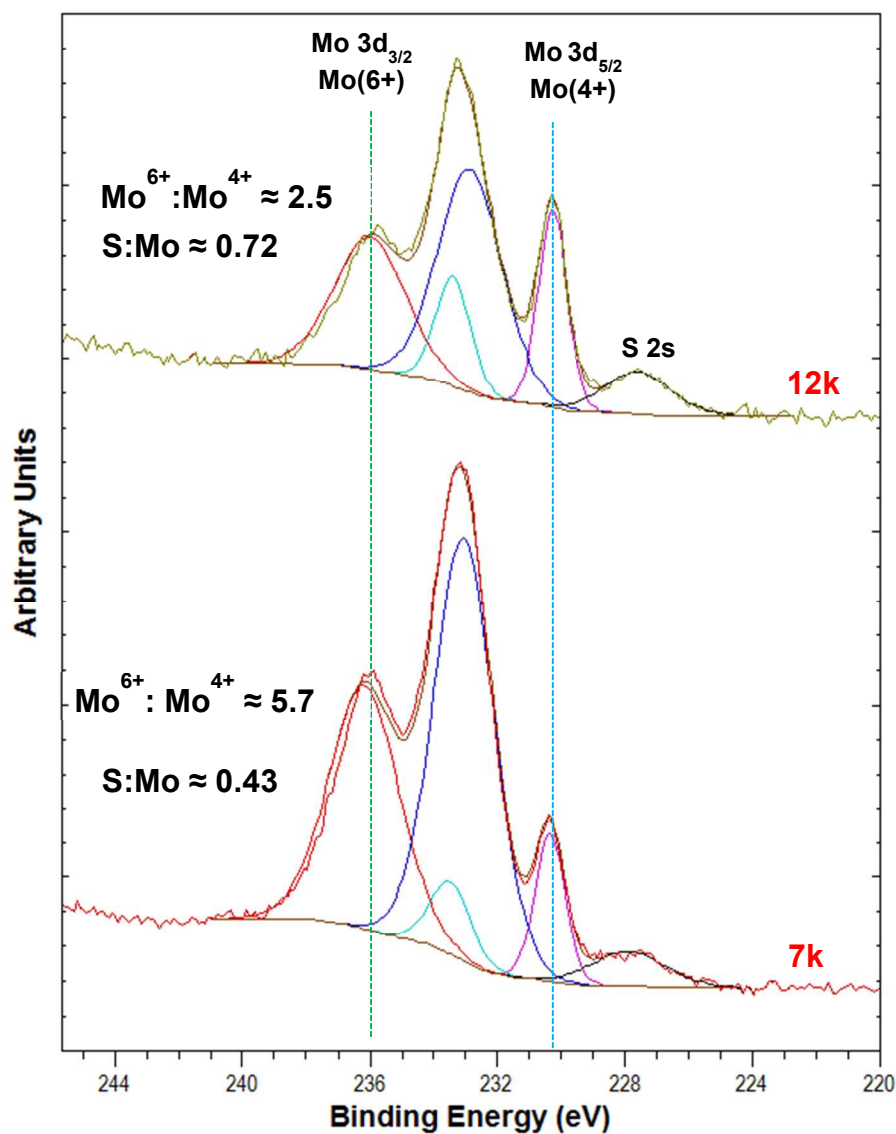


Figure S7. XPS Spectra of MoS₂ exfoliated in the presence of NMS. The extent of oxidation from Mo⁴⁺ (blue) to Mo⁶⁺ (green) is higher than that for samples exfoliated in the presence of H₂O.

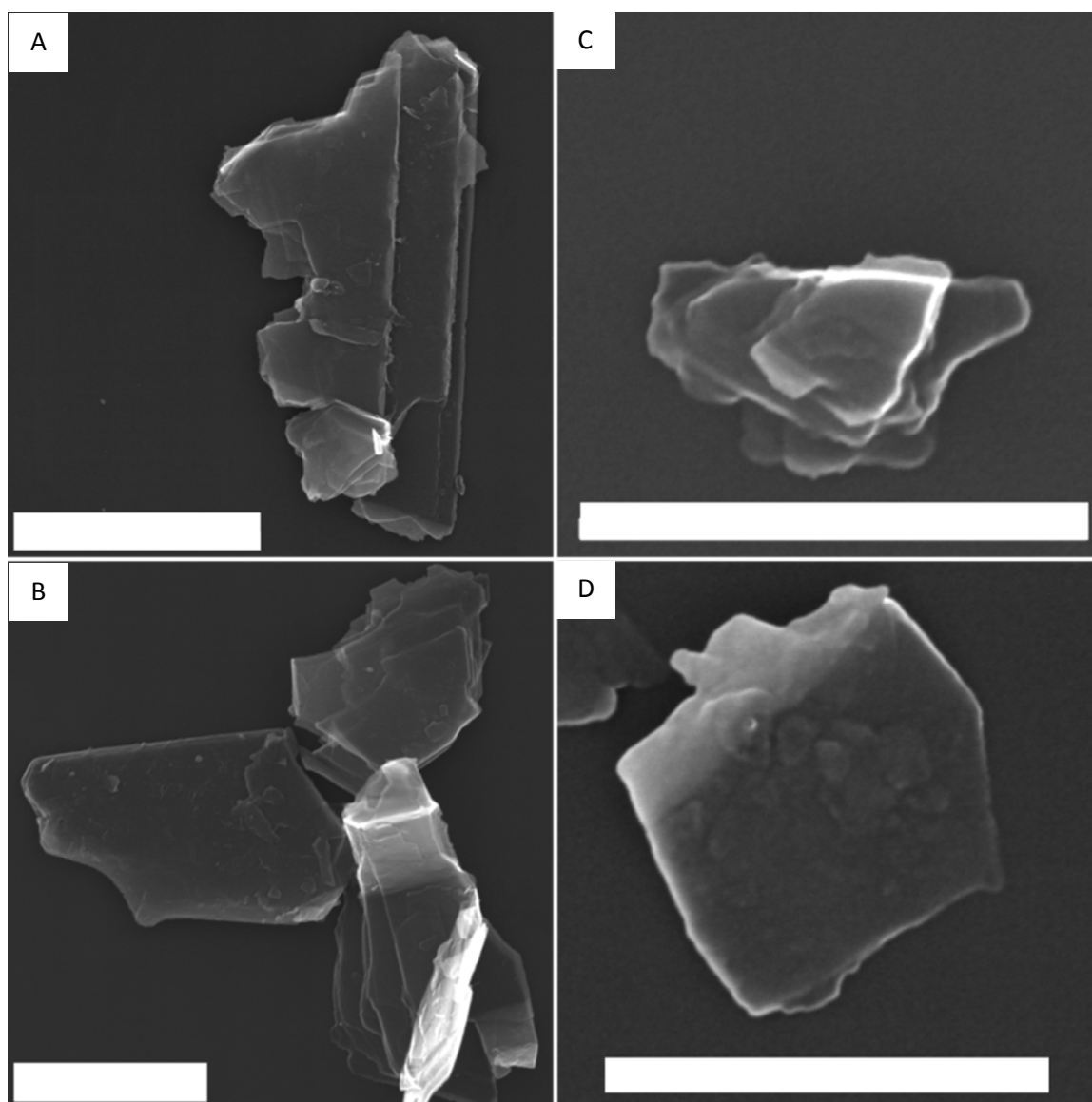


Figure S8. SEM micrographs of flakes isolated at different centrifugal speeds. **A, B)** Flakes isolated at 5,000 RPM (scale bar 1 μm). Note the stacking of smaller sized flakes on the basal surface of larger flakes. **C, D)** Flakes isolated at 12.7k RPM (scale bar 300 nm).

References

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