Electronic Supplementary Information for

Chemically Exfoliated ReS_2 Nanosheets

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Sample synthesis

Lithium intercalation was carried out in a standard Ar-filled glovebox with low vapor and oxygen levels (~1 ppm). ReS_2 was intercalated with lithium via a solvent-free method by reacting ReS_2 powder (0.1 g) with lithium borohydride (35 mg), following Kanatzidis et al.[S1] The following chemicals were used as received from commercial suppliers: rhenium disulfide (ReS_2, 99%) from Alfa Aesar and lithium borohydride ($LiBH_4$) from Sigma-Aldrich. Both powders were mixed to ensure homogeneity, then heated to 350 °C under flowing argon. After 3 days, the resulting black powder was immersed in Ar-bubbled water at a ratio of 1 mg per mL of the water. The solution turned completely dark in a few seconds. Sonication was then performed for one hour. Lithium cations and non-exfoliated ReS_2 were removed by centrifugation following the same protocol as we recently reported.[S2]

Electrochemical analysis

The electrodes for the HER measurements were prepared by simply drop casting the as-exfoliated solution (0.5 ml) onto conventional glassy carbon electrodes at room temperature. The measurements were performed after drying completely. HER measurements were carried out in a 0.5 M sulfuric acid (H_2SO_4) electrolyte solution. The reactivity of chemically exfoliated ReS_2 toward hydrogen evolution was measured using saturated calomel electrodes (SCE, BAS Inc.) and Pt electrodes (BAS Inc.) as reference and counter electrodes, respectively. The reference electrode was calibrated with respect to a reversible hydrogen electrode (RHE) using platinum wires as working and counter electrodes. In 0.5 M H_2SO_4, $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.256$ V. Electrochemical characterization was carried out using a classic three-electrode setup (Iviumstat electrochemical analyzer, Ivium Technology). Potential sweeps were performed with a 5 mV/s scan rate. Cyclic voltammetry (CV) from 0 V to –0.4 V (vs. RHE) was conducted to assess the electrochemical stability of the metastable 1T′ electrodes by monitoring the current density at –0.3 V.

TEM & STEM observation

Surface microstructure was characterized using a scanning electron microscope (SEM, JEOL JIB-4600F), and a transmission electron microscope (TEM, JEOL JEM-2100F), with double spherical aberration correctors (CEOS GmbH, Heidelberg, Germany). HAADF STEM imaging was performed at an acceleration voltage of 120 kV and collection angle between 100 and 267 mrad.

Additional TEM images

Figure S1 shows the morphology and quality of the exfoliated ReS_2 nanosheets in low-mag STEM images on a carbon mesh. The nanosheets are dispersed, and the size varies from 50 to 100 nm. Figure S2 shows a high-resolution STEM image of ReS_2 nanosheets annealed at 500 °C for 1 hour. The original crystal structure was recovered and the 1T structure with chains of Re clusters were confirmed.

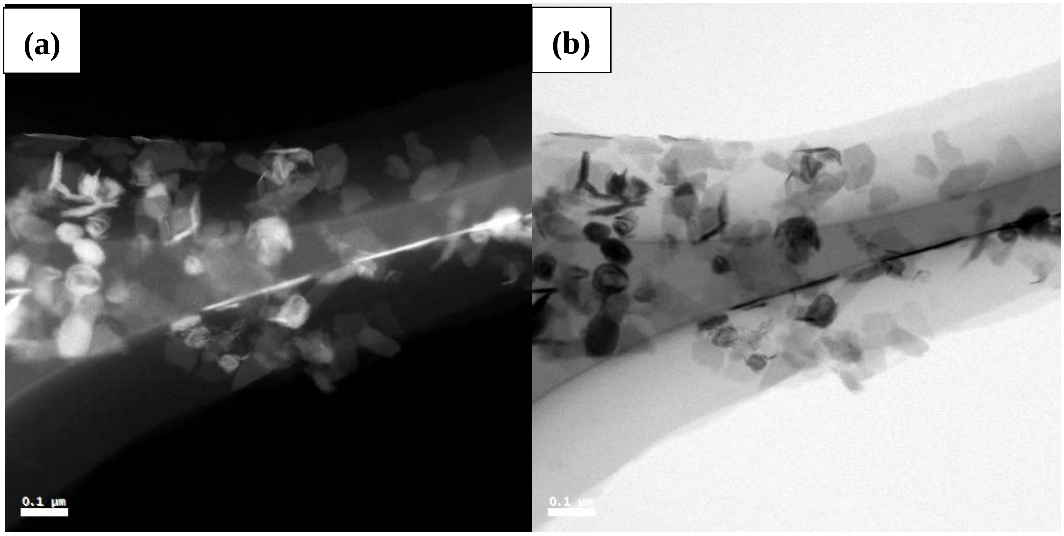

Figure S1. Low-mag STEM images of the exfoliated ReS_2nanosheets. (a) Dark-field image, and (b) corresponding bright-field image.

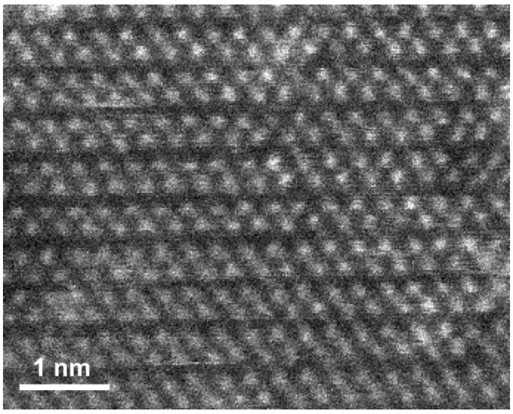

Figure S2. High-resolution STEM image of a ReS_2 nanosheet annealed at 500 °C for 1 hour.

AFM analysis

AFM data were obtained using a Vecco Instruments AFM system (CP-50-OL) in tapping mode with standard cantilevers with tip curvatures of <10 nm. Figures S3(a) and (b) show the AFM image and the height distribution of the individual exfoliated ReS_2 nanosheets. The sample was prepared by filtering a small volume (~1 mL) of dilute ReS_2 suspension to minimize overlap between individual sheets. The resulting film was nonhomogeneous due to partial aggregation. Regions of the sample where the sheets were isolated were imaged for step height analysis. The average thickness was 2.3 nm.

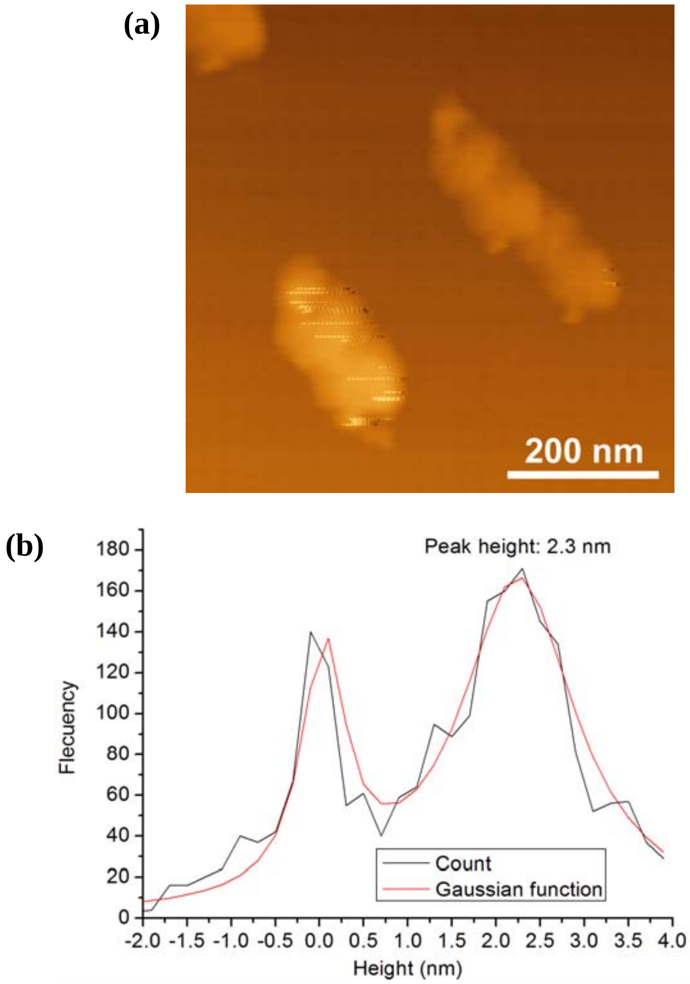

Figure S3. (a) AFM image and (b) height distribution of individual exfoliated ReS_2 nanosheets on a Si substrate. The peak at 0 nm height comes from the substrate.

X-ray diffraction

XRD profiles were obtained using a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation. As-received ReS_2 and Li_xReS_2 were measured in powder form. The peak positions marked in Figure S4, and the corresponding *d* spacings and expected planes, are summarized in Table S1. The (*h*, *k*, *l*) indexing was taken from a crystallographic database (CSD#052-0818). A small expansion of the interlayer spacing from (001) and (003) planes was expected, but this is not as significant as that present in

MoS_2.[S2] Therefore, Li intercalation and the corresponding exfoliation mechanism of ReS_2 needs further investigation.

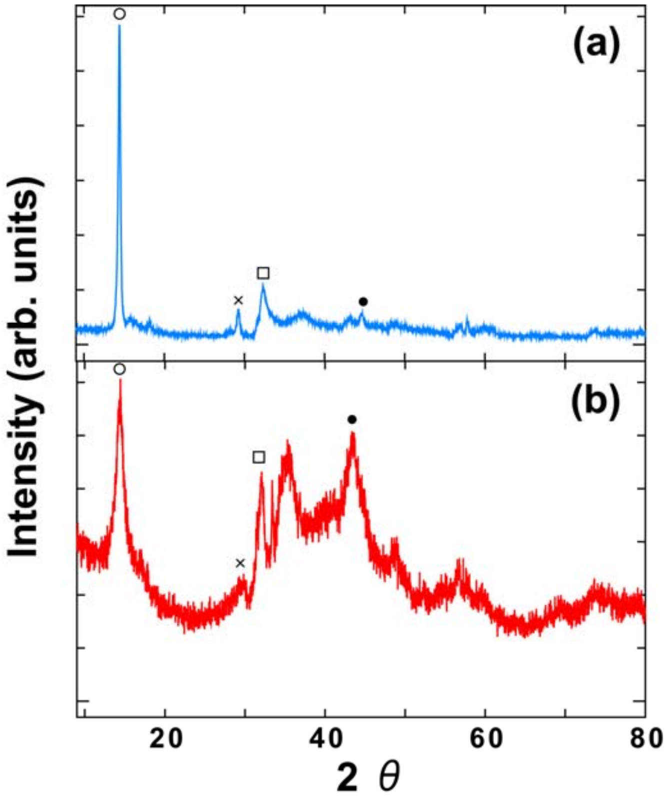

Figure S4. X-ray diffractogram of (a) as-received ReS_2 powder and (b) Li-intercalated ReS_2 (Li_XReS_2) powder.

Table S1. Peak positions marked in Figure S4, and the corresponding *d* spacings and interplanar distances for as-received and Li-intercalated ReS_2 powders.

As-received ReS_2			Li-intercalated ReS_2	
Angle (degree)	*d* (Å)	(*h*, *k*, *l*)	Angle (degree)	*d* (Å)
14.432	6.1322	(0, 0, 1)	14.13	6.261
29.26	3.050	(0, 0, 2)	29.71	3.028

32.26	2.773	(2, -2, 0)	32.09	2.787
44.59	2.0306	(0, 0, 3)	44.09	2.052

Zeta potential measurements

Zeta potentials of as-exfoliated ReS_2 nanosheets and as-received ReS_2 powders were measured using a Malvern Instrument Zetasizer Nano-ZS. Each sample was first dispersed to 0.1 mg/mL in DI water and sonicated for 30 min. 1 mL of the obtained dispersion was poured into a disposable capillary cell (Malvern, DTS1061) used for the measurement of zeta-potential. The values reported are an average of five independent measurements.

Table S2. Zeta potential values of as-exfoliated ReS_2 nanosheets and as-received ReS_2 powders in DI water of pH 7.8.

	Zeta-potential (ʃ , mV)
as-exfoliated ReS_2 nanosheet	-32.1 ± 0.5
as-received ReS_2 powder	-23.7 ± 1.7

X-ray photoelectron spectroscopy (XPS) measurements

The XPS spectra of the as-received ReS_2 powders and as-exfoliated ReS_2 nanosheets were measured by using an X-ray photoelectron spectroscope (AXIS ULTRA-DLD, Shimadzu) with Al Kα using an X-ray monochromator. Figure S5 shows the XPS spectra of the Re 4f and S 2p core level peak regions. After the exfoliation, the peaks of Re 4f shifted to 0.47 eV larger than that of bulk, indicating that the Re atoms were more positively charged, and small amounts of metallic-state Re were found at the shoulders of the peaks. The deconvolution of the spectra of S 2p revealed two new peaks after exfoliation, which may have been caused by the mixture of different atomic configurations due to the transformed superlattice 1T′.

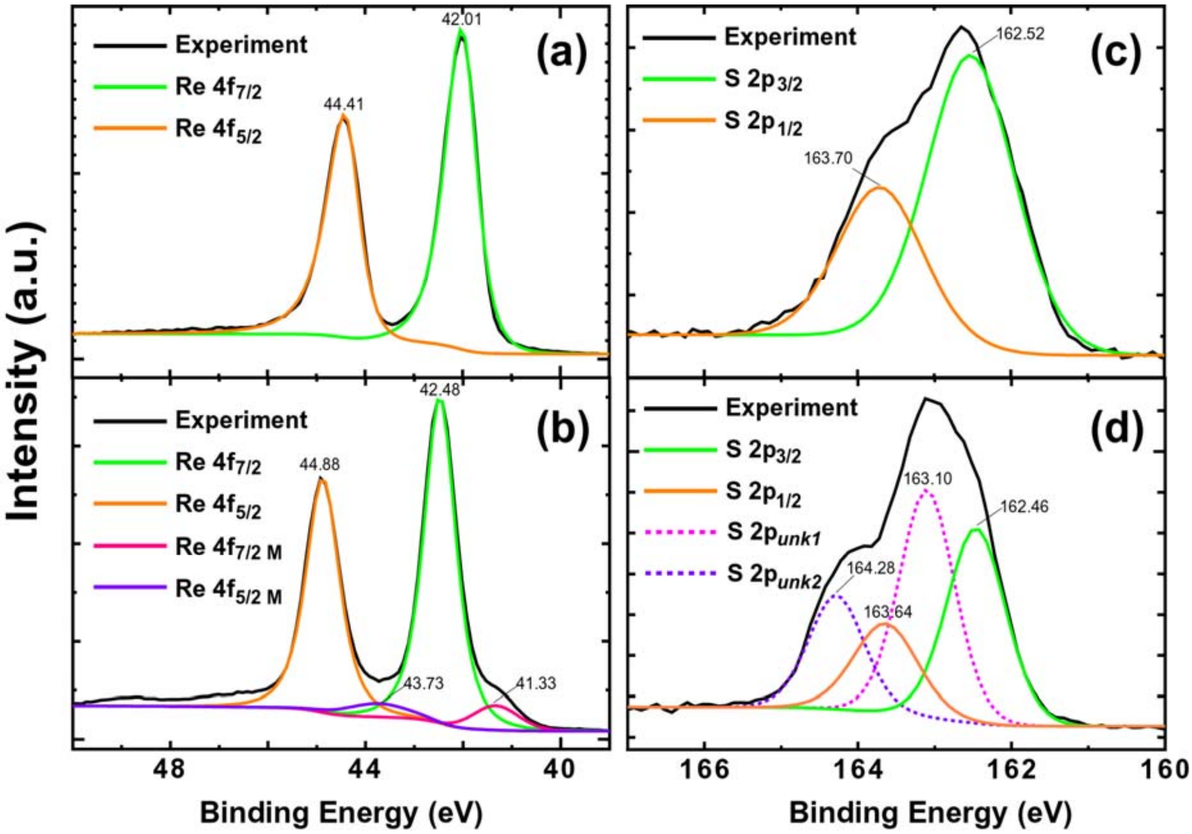

Figure S5. XPS spectra showing Re 4f and S 2p core level peak regions for [(a) and (c)] as-received ReS_2 powders and [(b) and (d)] as-exfoliated ReS_2 nanosheets. The values (eV) at the peak positions are indicated.

Optical analysis

Raman and PL spectra were recorded using a Raman microscope (Renishawin Via RM 1000) with an incident wavelength of 514.5 nm at room temperature. Raman and PL spectra were acquired under the same conditions, i.e. acquisition time and optical settings, for comparison purposes. The probe laser beam is ~3 μm in diameter.

The exfoliated nanosheets are smaller than the probe size, and the spectra were acquired from the restacked nanosheets because the individual nanosheets are invisible under an optical microscope. To avoid possible sample damage by laser irradiation, the laser power was kept to a minimum.

Additional PL analysis

PL spectra were collected from different areas of the as-exfoliated ReS_2 nanosheets supported on an oxidized Si substrate. The optical microscope images in Figure S6 show the analyzed areas (red circles) for each PL spectra taken from (a) and (b). The ReS_2 nanosheets did not show hot luminescence from the thin and well-dispersed area of (a), but large PL peaks were obtained from the aggregated areas of (b). The spectrum from the bulk (as-received powders) is shown for comparison; the acquisition conditions were the same. Therefore, the signal intensity is closely related to the area of nanosheets in the probed regions because, unlike MoS_2, ReS_2 nanosheets did not show hot luminescence resulting from indirect to direct bandgap transitions or a dependence on the number of layers.

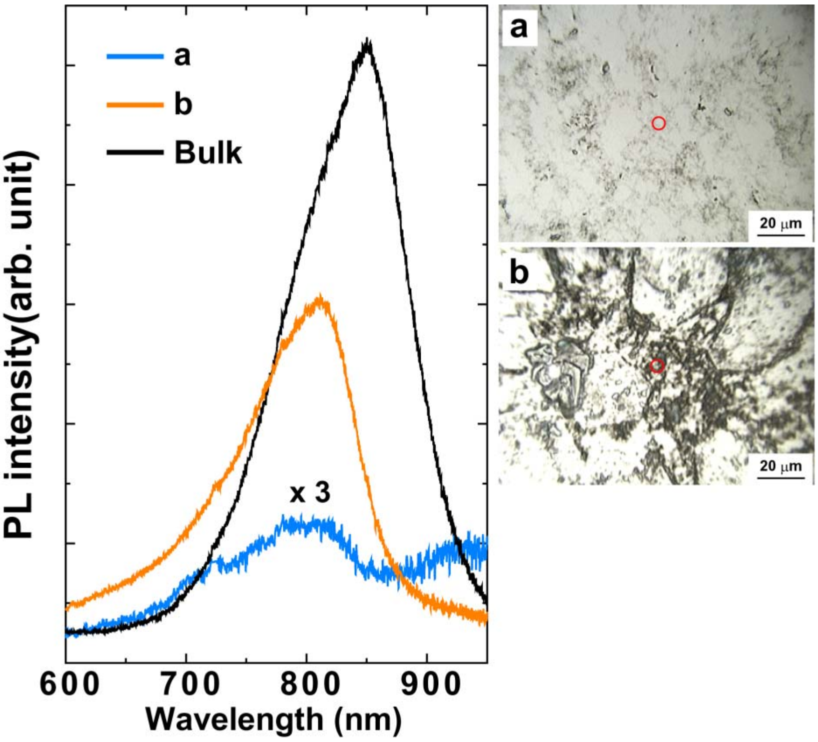

Figure S6. PL spectra collected from different areas ((a) and (b)) of the as-exfoliated ReS_2 nanosheets on an oxidized Si substrate. The spectrum collected from the bulk (as-received powders) is shown for comparison.

References

(S1) Tsai, H. L.; Heising, J.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 879–882.

(S2) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M. W.; Chhowalla, M. *NanoLett.***2011**, *11*, 5111–5116.