Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Exfoliated semiconducting pure 2H-MoS_2 and 2H-WS_2 assisted by chlorosulfonic acid

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Experimental Section

MoS_2 and WS_2 powders, NMP (>99% purity), DMF (>99.8 % purity) and chlorosulfuric acid (>98% purity) were purchased from Sigma Aldrich. All chemicals were used as received without further purification. Tip sonication was performed with a Bandelin Sonoplus Ultrasonic Homogenizer HD 3200 equipped with a flat head probe (VS70T), running at 35% of the maximum power (250 W). Centrifugation was performed using an Eppendorf 5702 at 3500 rpm-4400 rpm. UV-visible spectra were recorded on a Perkin-Elmer (Lamda 750, UV-vis-NIR spectrophotometer), while Raman characterization was carried out at room temperature with a Renishaw confocal spectrometer using Ar – Laser at 514 nm and 633 nm. Fluorescence spectra were taken on a Fluorolog-3 JobinYvon-Spexspectrofluorometer (model GL3–21). The XPS measurements were performed in a VERSAPROBE PHI 5000 from Physical Electronics, equipped with a Monochromatic Al Kα X-Ray source. The energy resolution was 0.7 eV. For the compensation of built up charge on the sample surface during the measurements a dual beam charge neutralization composed of an electron gun (~1eV) and an Argon ion gun ($\leqslant$ 10 eV) was used. The samples for XPS measurements were supported on a copper conductive double face tape compatible with UHV. For the XPS analysis, we calibrated our system using the carbon sp^2 C-C peak at 284.6 eV. The CASA XPS software (CASAXPS Software Ltd., UK) was used for curve fitting. The spectra were resolved into their components after an integrated Shirley background subtraction. Curve-fitting parameters (FWHM and Gaussian/Lorentzian ratio) were determined from reported reference spectra[1] The spectra were fitted with symmetrical Gaussian/Lorentzian peaks, keeping the FWHM and the Gaussian(80%)/Lorentzian(20%) ratio constant and fitting the energy of the peaks and their heights. Peak height of Mo 3d$_{3/2}$ and W 4f$_{5/2}$ were constrained based on known height ratios, 0.69 of the Mo 3d$_{5/2}$ height and 0.75 of the W 4f$_{7/2}$ height. The doublet S 2p$_{1/2}$ was assigned at 1.16 eV higher than the S 2p$_{3/2}$, and constrained based on known height ratio, to 0.511 of S 2p$_{3/2}$, in both WS_2 and MoS_2 samples. The STEM imaging studies were performed on probe-corrected FEI Titan Low-Base 60-300 microscope operating at 200 kV (fitted with a X-FEG® gun, a Cs-probe corrector (CESCOR from CEOS GmbH)). The dose was reduced to avoid beam damage.[2] HR-

STEM imaging was performed using a high-angle annular dark field (HAADF) detector. The inner and outer angles of the HAADF were around 65 and around 200 mrad, respectively. The STEM convergence semi-angle was 25 mrad. In order to reduce the noise and then to increase the image quality a Wiener filter has been applied to these STEM images. For sake of clarity, false-coloured images were employed.

Exfoliated TMDs: Chlorosulfuric acid (2 mL) was added to bulk TMDs (150 mg) and the mixture was sonicated for 2h. In the resultant raw dispersion, distilled water was carefully added under vigorous stirring at 0 ^oC, until the production of fuming HCl stopped. In the next step, the dispersion was filtered over PTFE filter (pore size 0.1μm) and washed several times with distilled water. Before the filter was completely dried, the residual material was transferred to a beaker, NMP (150 mL) was added and the mixture was probe-sonicated (1h, 35% amplitude, 0 ^oC). Following centrifugation, the material was left overnight to settle and the exfoliated TMDs were obtained from the supernatant. The same procedure was applied to obtain exfoliated TMDs in DMF and in distilled water.

References

[1] F. S. Ohuchi, W. Jaegermann, J C. Pettenkofer, B. A. Parkinson, *Langmuir* **1989,** 5**,** 439-442.

[2] R. Arenal and A. Lopez-Bezanilla, *ACS Nano* **2014**, *8*, 8419-8425.

Table S1. Solubility values of exfoliated MoS_2 and WS_2.

Solvent	**Exfoliated MoS_2**	**Exfoliated WS_2**
NMP	8.9 mg/L	6.1 mg/L
DMF	3.1 mg/L	4.8 mg/L
H_2O	2.2 mg/L	1.0 mg/L

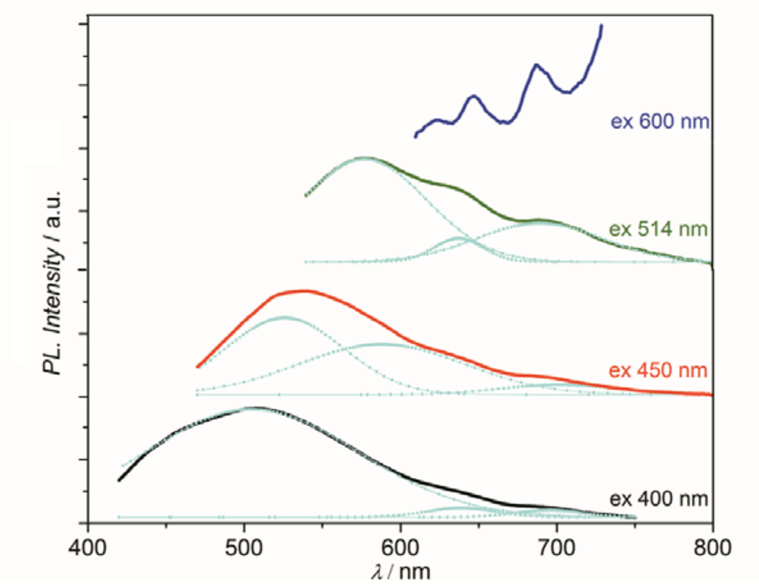

Figure S1. Fluorescence emission spectra of exfoliated MoS_2, obtained in NMP upon various excitation wavelengths in the range 400-600 nm.

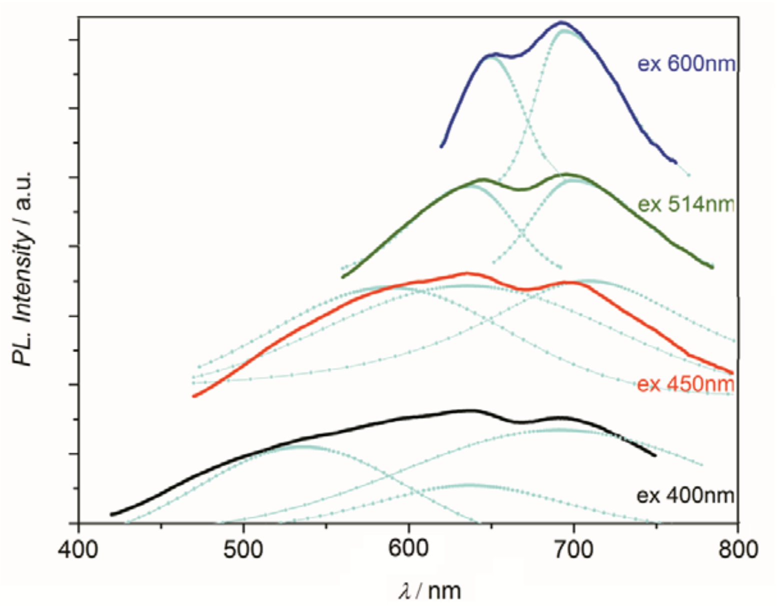

Figure S2. Fluorescence emission spectra of exfoliated MoS_2, obtained as thin-films deposited on Si/SiO_3 glass, upon various excitation wavelengths in the range 400-600 nm.

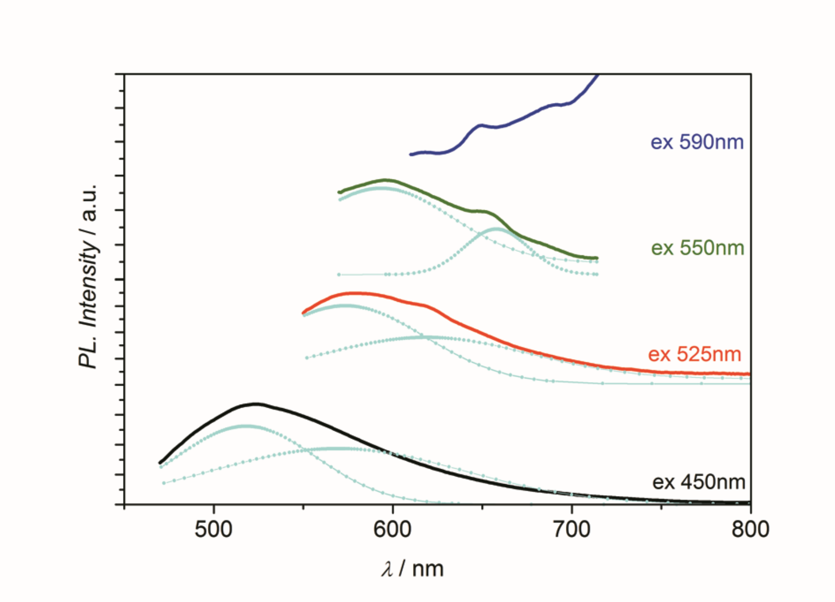

Figure S3. Fluorescence emission spectra of exfoliated WS_2, obtained in NMP upon various excitation wavelengths in the range 450-590 nm.

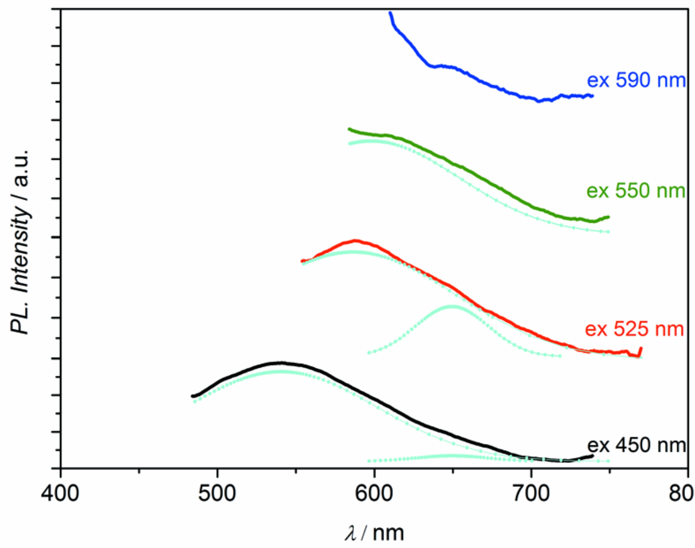

Figure S4. Fluorescence emission spectra of exfoliated WS_2, obtained as thin films deposited on Si/SiO_3 glass upon various excitation wavelengths in the range 450-590 nm.

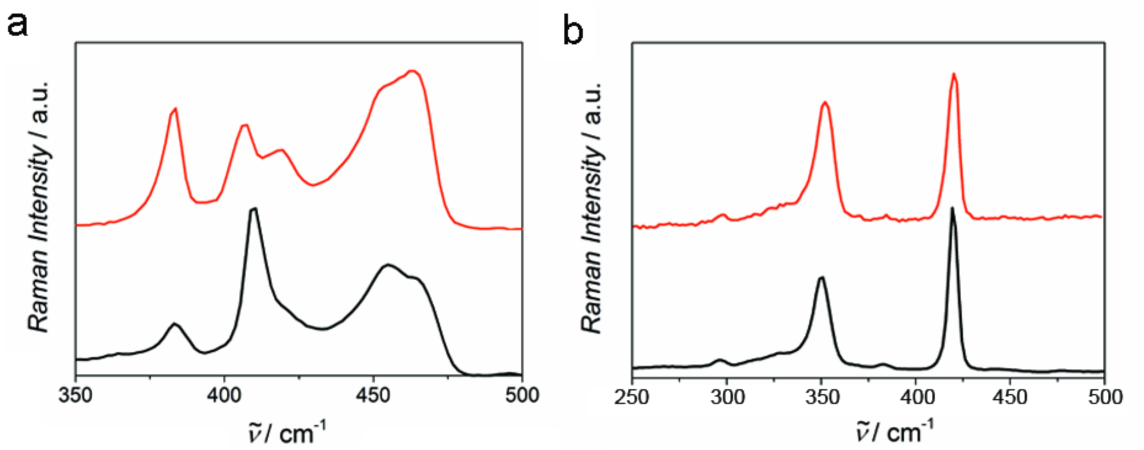

Figure S5. Raman spectra of exfoliated MoS_2 (red) as compared with bulk MoS_2 (black), obtained at (a) 633 nm, and (b) 514 nm excitation. The blue dotted lines are the Lorentzian fittings of the E^1_{2g} and A_{1g} modes.

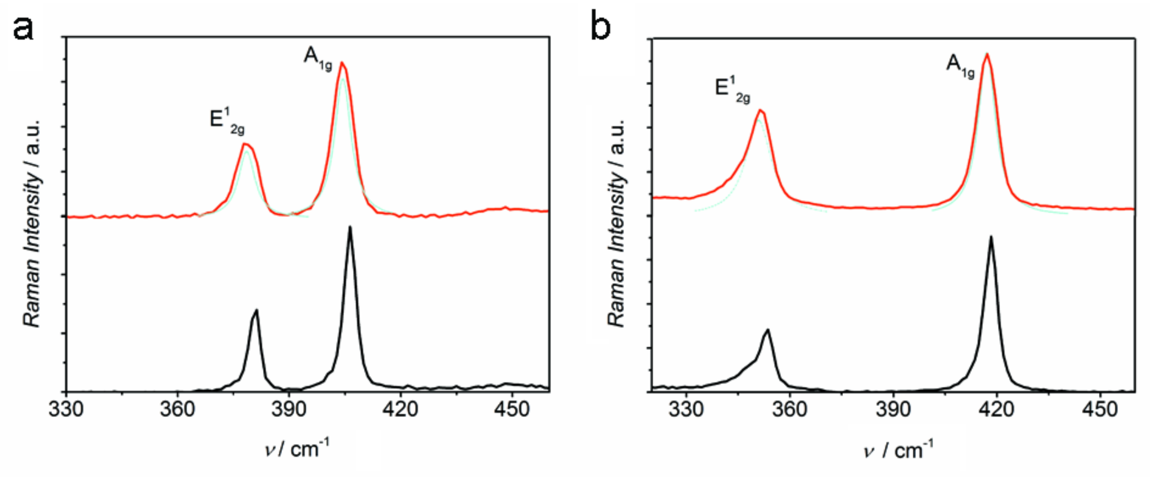

Figure S6. Raman spectra of exfoliated WS_2 (red) as compared with bulk WS_2 (black), obtained at (a) 633 nm, and (b) 514 nm excitation. The blue dotted lines are the Lorentzian fittings of the E^1_{2g} and A_{1g} modes.