

Supporting information

Photoluminescence Emission Induced by Localized States in Halide-Passivated Colloidal Two-Dimensional WS₂ Nanoflakes

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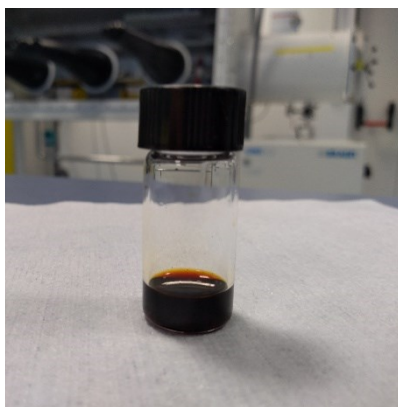


Figure S1. Picture of a concentrated (4 mg/mL) solution of Br⁻ passivated WS₂ NFs in NMF

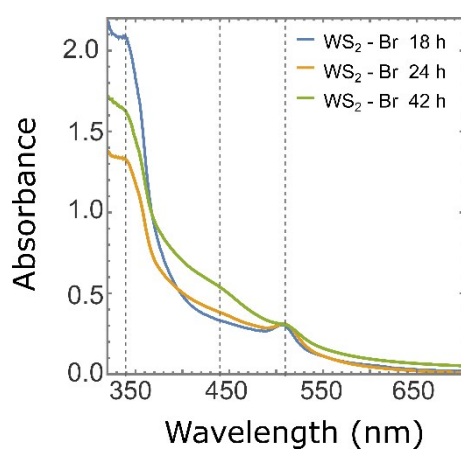


Figure S2. Evolution of UV-vis absorption spectra of Br⁻ passivated WS₂ NFs as a function of the sonication time: 18h, 24 h, and 42 h. Each absorption spectrum is normalized to the A exciton peak.

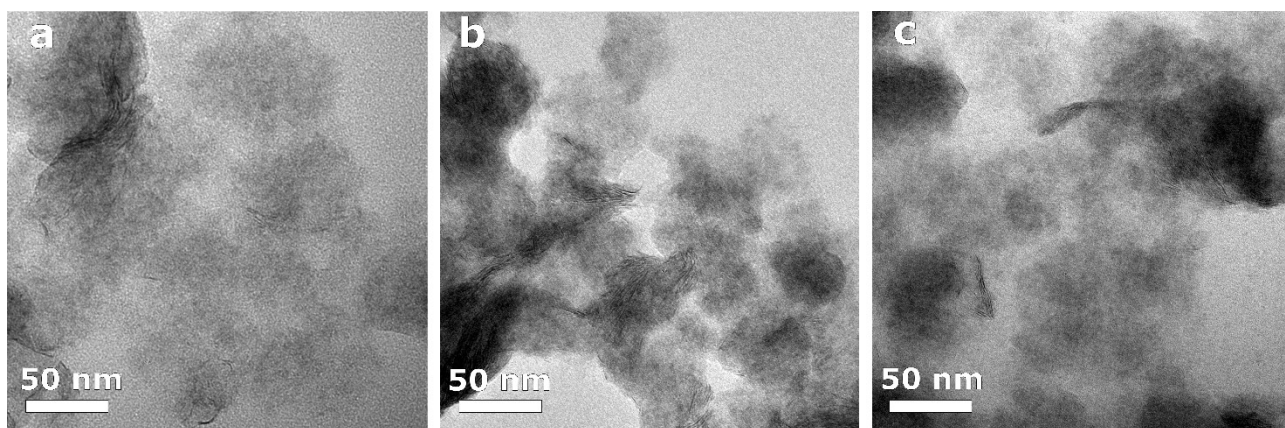


Figure S3. TEM images of Br-passivated WS₂ NFs after (a) 18h , (b) 24 h, and (c) 42 h of sonication.

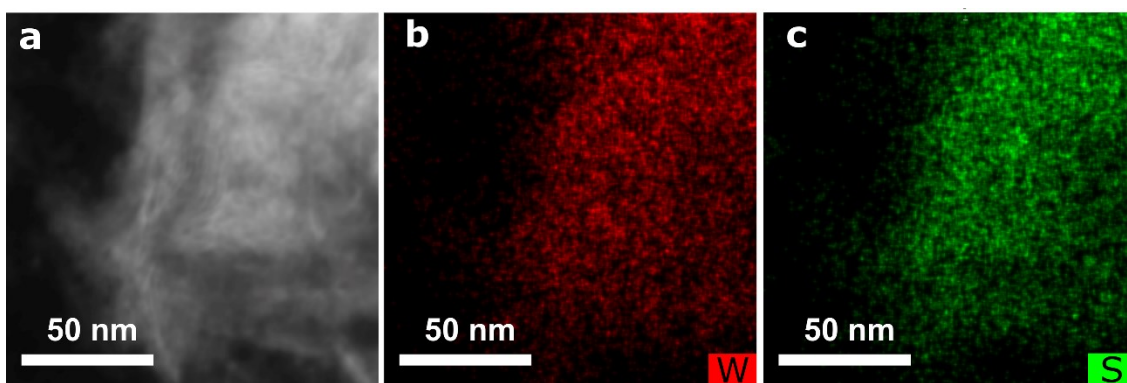


Figure S4. (a) HAADF-STEM image of Br-passivated WS_2 - NFs with the corresponding elemental EDX maps for (b) W and (c) S.

	W (at. %)	S (at. %)	Br (at. %)	S : W ratio
Pristine WS_2 NFs	42.5	57.5	0	1.4
WS_2 - Br NFs	37.7	58.4	3.9	1.6

Table S1. Atomic concentration of the as-synthesized and Br⁻ passivated WS_2 NFs measured by the quantification of the EDX maps in Supplementary Figure 5. The selected energy transitions for atomic percentage quantification were L= 8.4 eV, K= 2.3 eV, K= 11.9 eV for W, S and Br respectively. The uncertainty on the EDX analysis was estimated to be 3-4%.

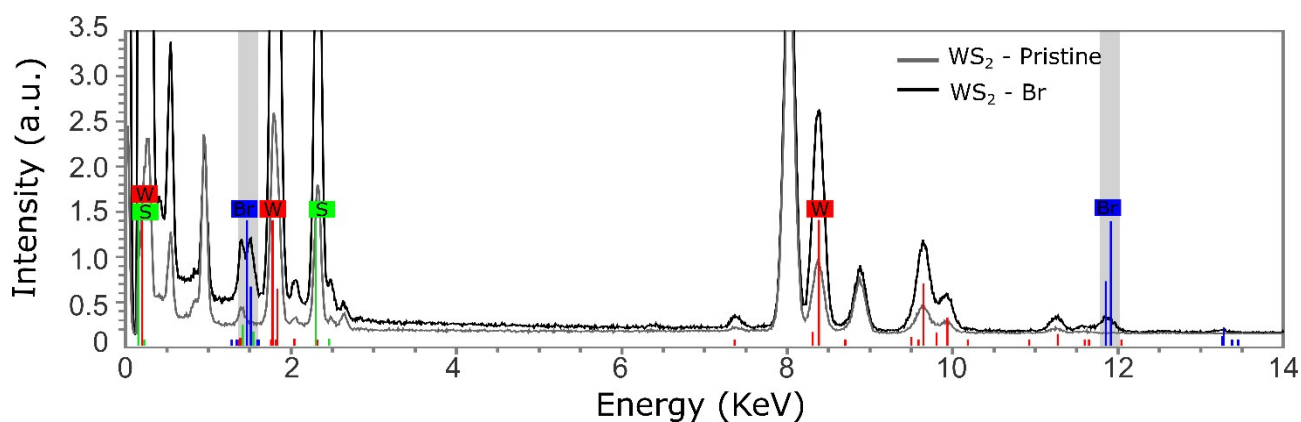


Figure S5. EDX spectra for the pristine and Br passivated WS_2 NFs.

XPS peak	Chemical state	Binding Energy (eV)	WS ₂ Pristine	WS ₂ Sonicated	WS ₂ Br
W 4f _{7/2}	W-S	32.4	3.3 ± 0.3	5.0 ± 0.3	0.12 ± 0.03
	W-O	34.1 (+1.7)	0.76 ± 0.05	1.6 ± 0.1	0.05 ± 0.01
	WO ₃	36.2 (+3.8)	0.42 ± 0.05	0.90 ± 0.05	-
	W-Br/W- O ₃	35.7 (+3.3)	-	-	0.04 ± 0.01
Br 3d _{5/2}	Br 3d	69.2	-	-	0.57 ± 0.07
S 2p _{3/2}	S-O	168	-	-	-
	S-W	162.2	7.7 ± 0.5	13.6 ± 0.8	0.61 ± 0.08
C 1s	C 1s	284.8	78.4 ± 0.9	71.1 ± 0.9	86.3 ± 0.9
O 1s	-	532	6.2 ± 0.5	3.4 ± 0.4	4.9 ± 0.3
In 3d _{5/2}	In-O	446.6	0.98 ± 0.08	-	1.2 ± 0.1
N 1s	-	401.1	2.2 ± 0.2	4.5 ± 0.2	1.7 ± 0.2

Table S2. Chemical composition (at. %) and chemical states obtained by XPS analysis of pristine, sonicated and passivated WS₂ NFs samples.

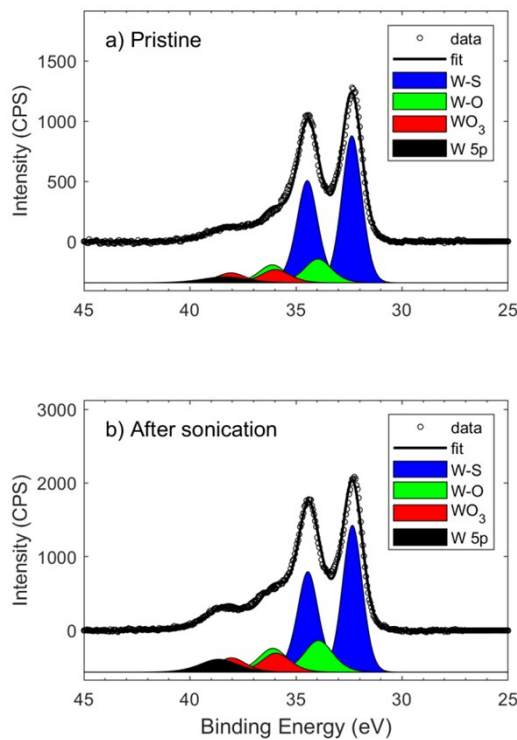


Figure S6. W 4f signal from (a) as synthesized WS₂ NFs and (b) WS₂ NFs after 24 h hour of sonication in NMF.

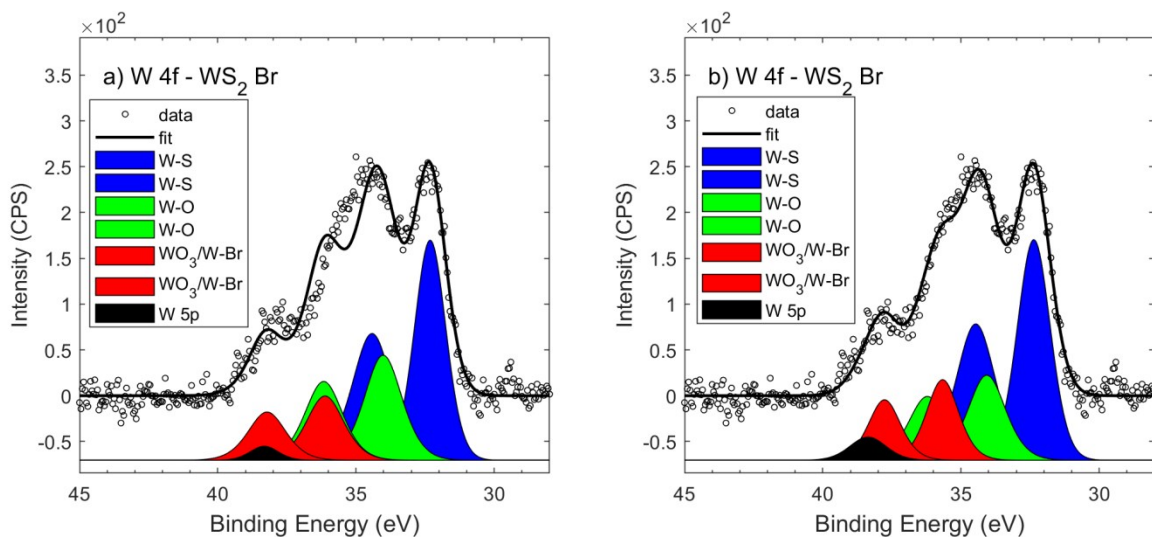


Figure S7. W 4f signal from Br-passivated WS₂ NFs (a) fitted with the same component in the same position of pristine WS₂ NFs, reduced chi square 0.396 and (b) by optimizing the position of WO₃/W-Br group, reduced chi square 0.197.

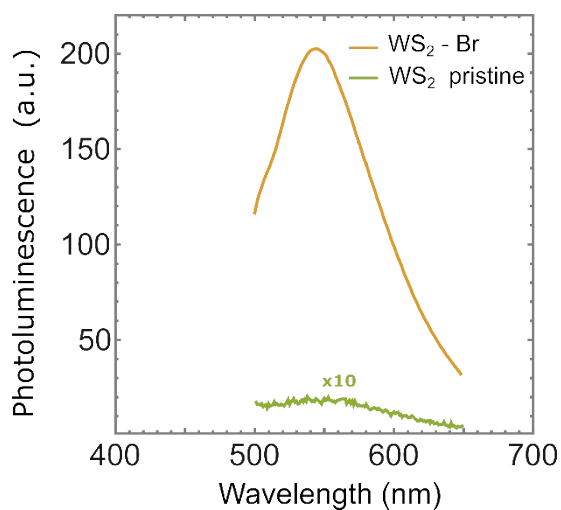


Figure S8. Photoluminescence spectra of pristine and Br-passivated WS₂ NFs.

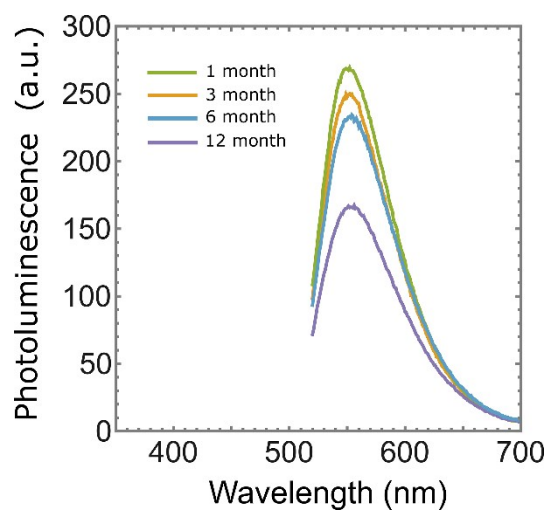


Figure S9. Photoluminescence spectra of Br⁻ passivated WS₂ NFs after several months of storage in air. We record a significant photoluminescence reduction only after 12 months of air exposure.

Passivation of WS₂ nanoflakes with I⁻ ions

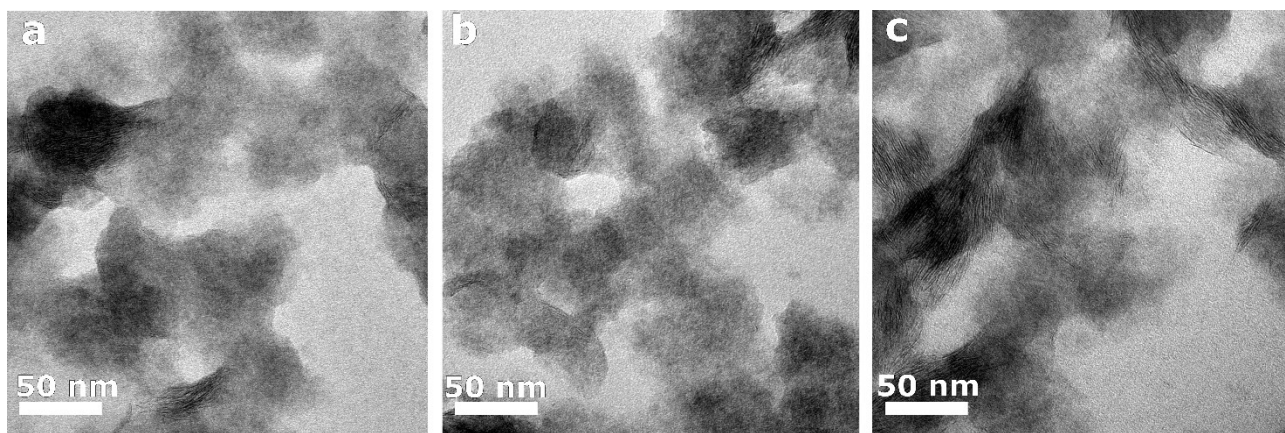


Figure S10. TEM images of I⁻ passivated WS₂ NFs after (a) 18h, (b) 24 h, and (c) 42 h of sonication.

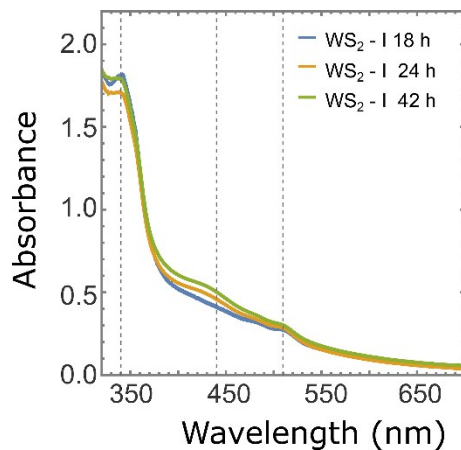


Figure S11. Evolution of UV-vis absorption spectra of I-passivated WS₂ NFs after 18h, 24 h, and 42 h of sonication

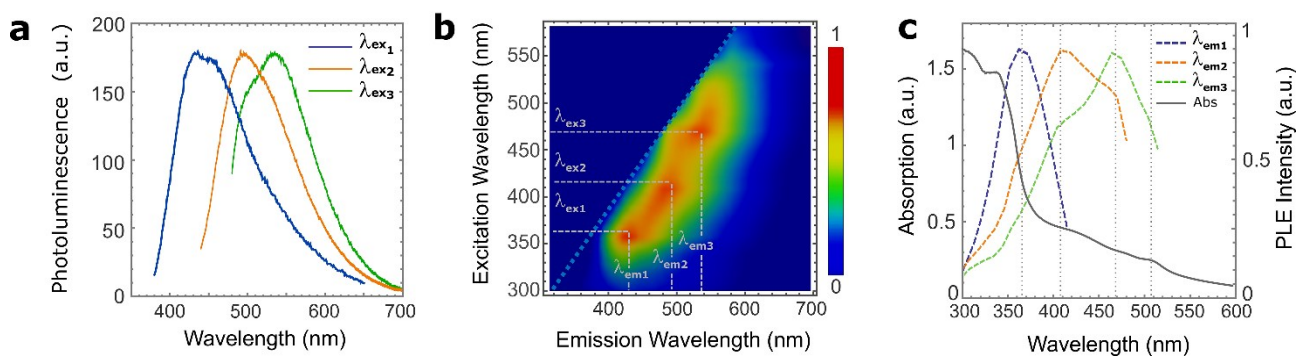


Figure S12. (a) PL spectra of I-passivated WS₂ NFs at excitation wavelengths of 380 nm (λ_{em1}), 430 nm (λ_{em2}), and 470 nm (λ_{em3}). (b) PLE intensity map. (c) PLE spectra extracted from PLE map at detection wavelength corresponding to stronger PL emission signals (430 nm, 490 nm and 530 nm). The absorption spectrum is also shown for comparison.

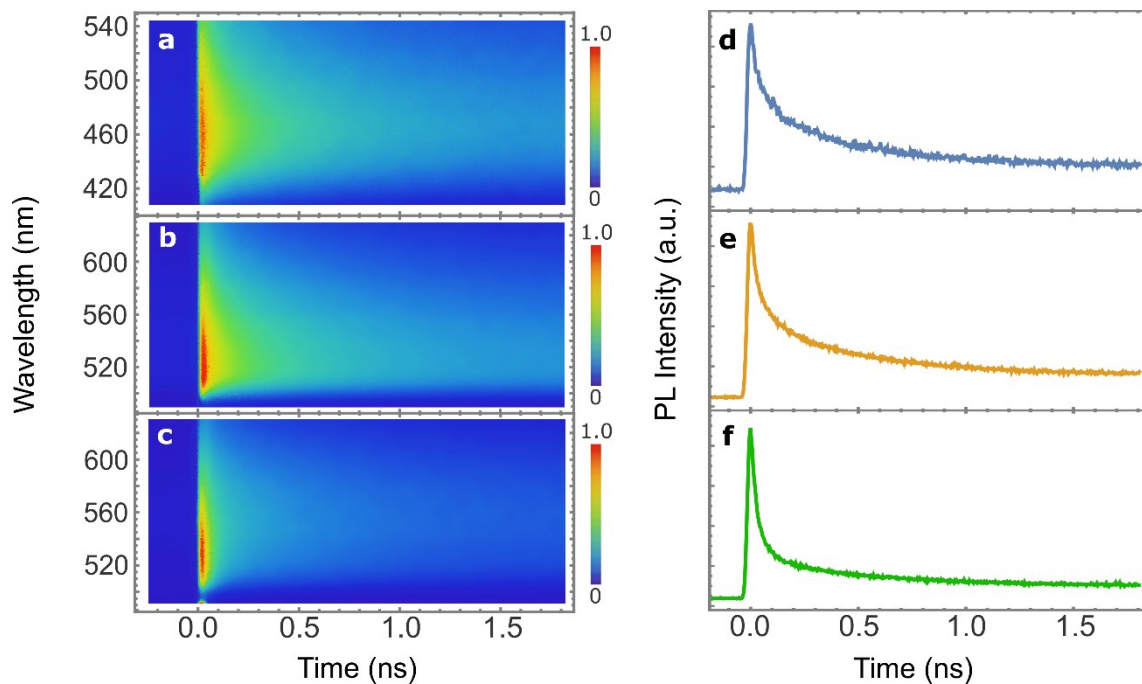


Figure S13. TRPL from I⁻ passivated WS₂ NFs after 24 h of sonication. (a,b,c) TRPL emission maps of I⁻ passivated WS₂ NFs for excitation wavelength of 380 nm, 430 nm, 470 nm, respectively; and (d,e,f) relative PL decay transients at detection wavelength at 530 nm.

Passivation of WS₂ nanoflakes with Cl⁻ ions

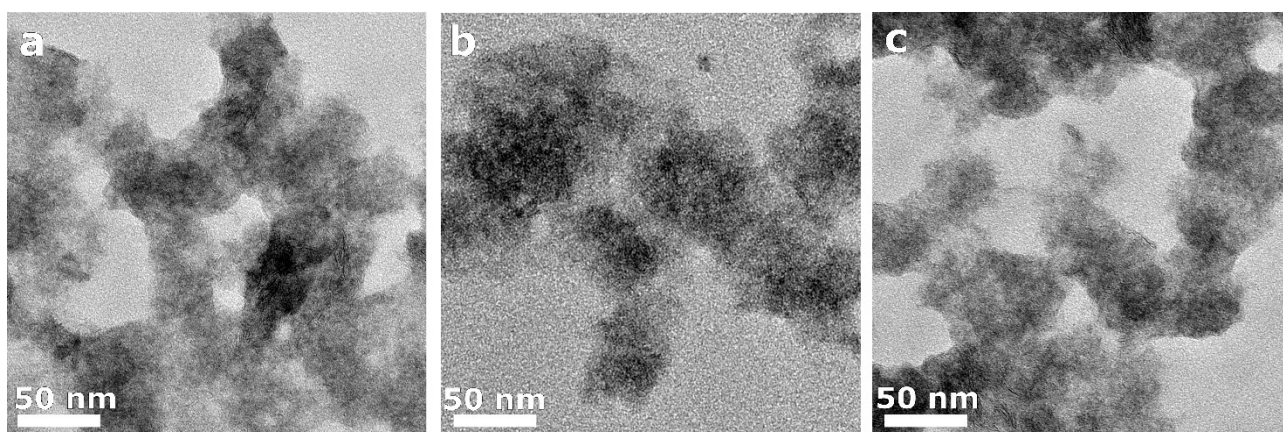


Figure S14. TEM images of Cl⁻ passivated WS₂-Cl NFs after (a) 18h, (b) 24 h, and (c) 42 h of sonication.

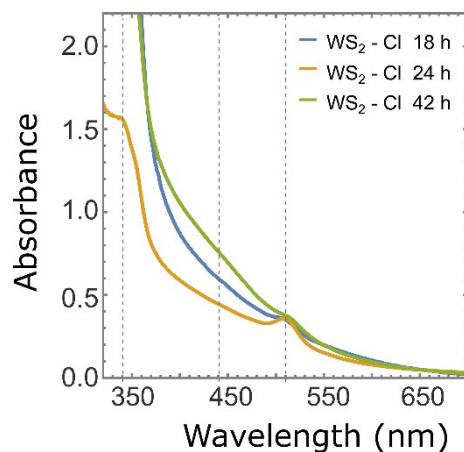


Figure S15. Evolution of UV-vis absorption spectra of Cl⁻ passivated WS₂ NFs after 18h, 24 h, and 42 h of sonication

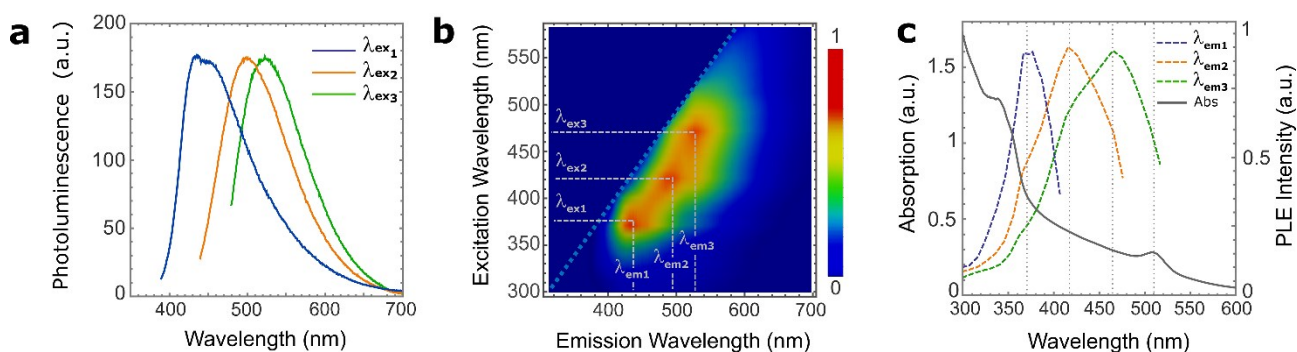


Figure S16. (a) PL spectra of Cl⁻ passivated WS₂ NFs at excitation wavelengths of 380 nm (λ_{em1}), 430 nm (λ_{em2}), and 470 nm (λ_{em3}). (b) PLE intensity map. (c) PLE spectra extracted from PLE map at detection wavelength corresponding to stronger PL emission signals (430 nm, 490 nm and 530 nm). The absorption spectrum is also shown for comparison.

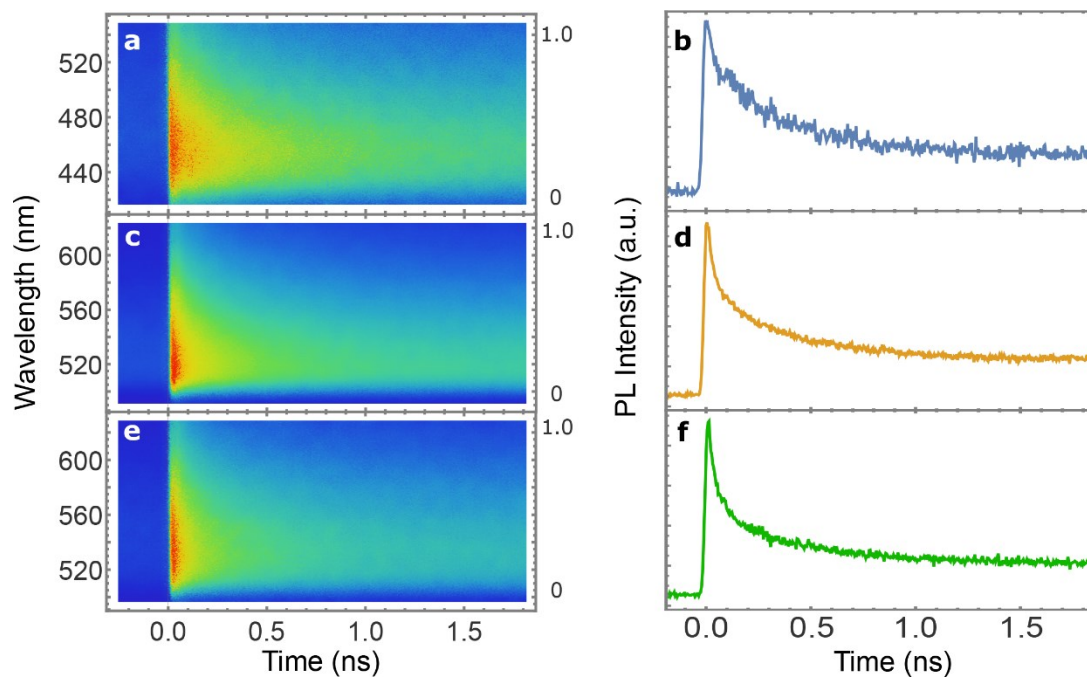


Figure S17. TRPL from Cl⁻ passivated WS₂ NFs after 24 h of sonication. (a,c,e) TRPL emission maps of Cl⁻ passivated WS₂ NFs for excitation wavelength of 380 nm, 430 nm, 470 nm, respectively; and (b,d,f) relative PL decay transients at a detection wavelength at 530 nm.

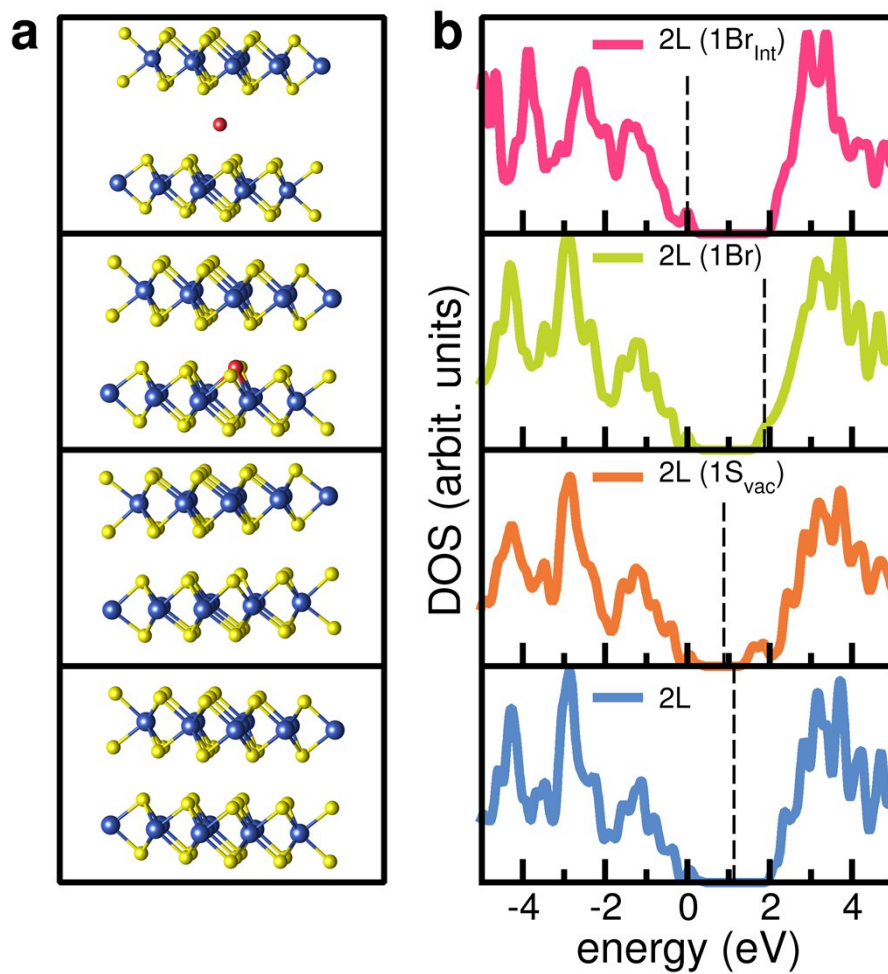


Figure S18. (a) Atomic structure and (b) density of states for WS₂ double layer (2L) with and without a single defect. From bottom to top: no defects; one S vacancy (1S_{vac}), one substitutional Br atom (1Br); and one interstitial Br atom (1Br_{int}).

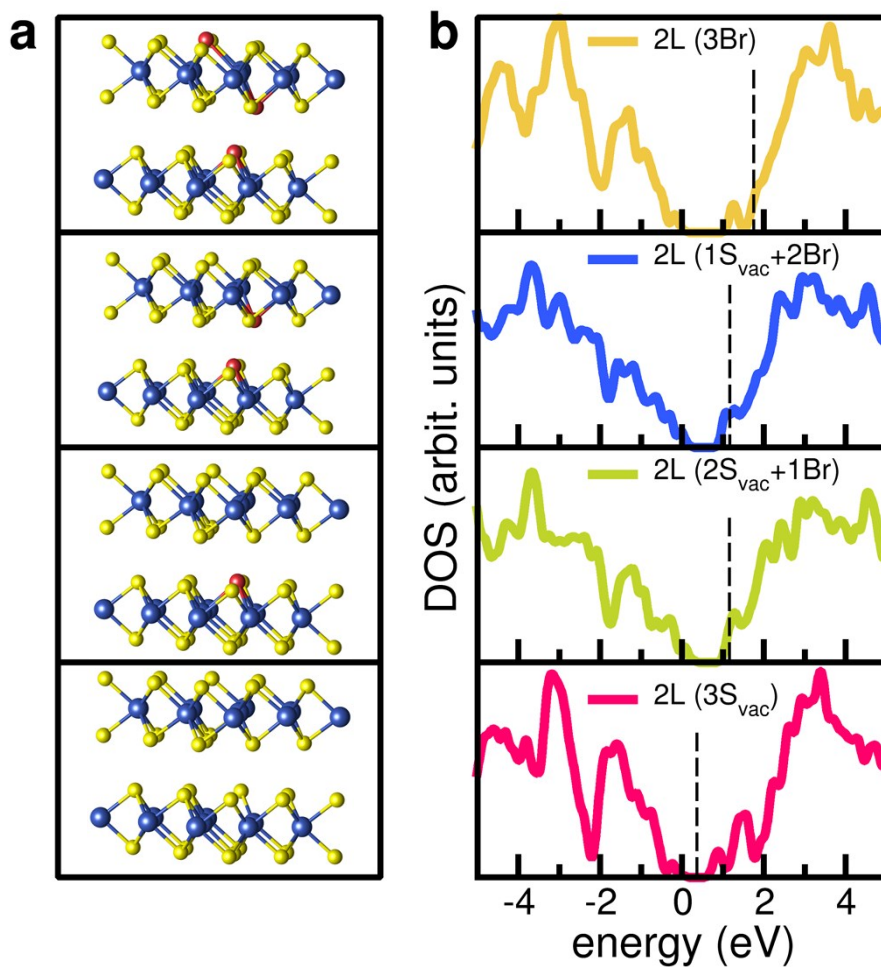


Figure S19. (a) Atomic structure, (b) density of states, and (c) absorption spectra for WS₂ double layer (2L) with three defects. From bottom to top: three S vacancy (3S_{vac}), two S vacancy and one substitutional Br atom (2S_{vac}+1Br), one S vacancy and two substitutional Br atoms (1S_{vac}+2Br), three substitutional Br atoms (3Br).