

Electronic Supplementary Information

Bidirectional doping of two-dimensional thin-layer transition metal dichalcogenides by soft ammonia plasma

Pu Tan,^{#,a} Kaixuan Ding,^{#,a} Xiumei Zhang,^b Zhenhua Ni,^c Kostya (Ken) Ostrikov,^d Xiaofeng Gu,^a Haiyan Nan^{*,a} and Shaoqing Xiao^{*,a}

a. Engineering Research Center of IoT Technology Applications (Ministry of Education), Department of Electronic Engineering, Jiangnan University, Wuxi 214122, China. Email: xiaosq@jiangnan.edu.cn; Jnanhaiyan@jiangnan.edu.cn

b. School of Science, Jiangnan University, Wuxi 214122, China.

c. Department of Physics and Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 211189, China.

d. School of Chemistry and Physics and QUT Centre for Materials Science, Queensland University of Technology (QUT), Brisbane QLD 4000, Australia.

These authors contributed equally to this paper.

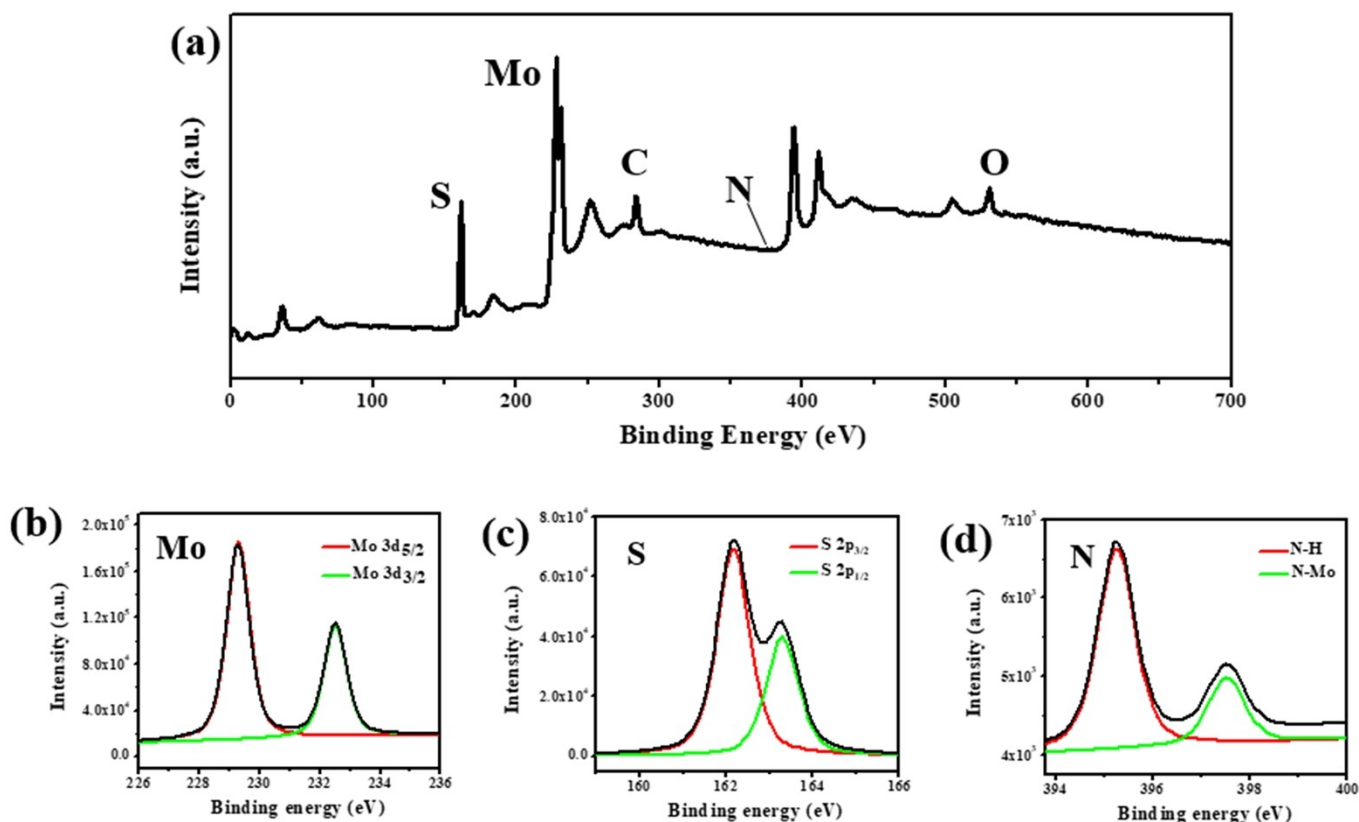


Figure S1 XPS characterization of the plasma-treated bulk MoS₂ sample. (a) XPS full spectrum. (b), (c) and (d) are the fitting diagrams of the high-resolution XPS spectra corresponding to the Mo, S, and N elements, respectively. The RF power of the soft NH₃ plasma is 10 W, and the processing time is 1 minute.

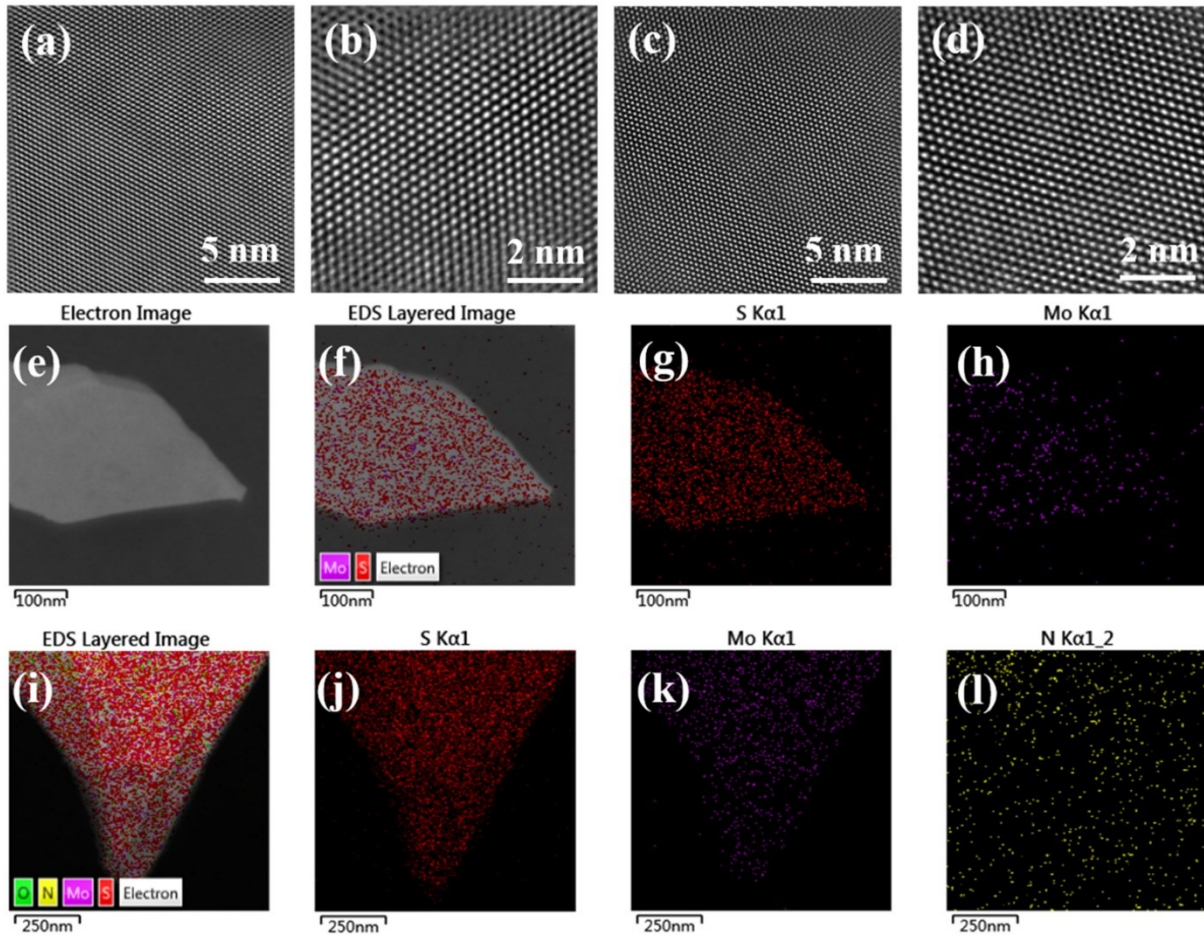


Figure S2 The TEM characterization of another thin-layer MoS₂ sample before and after NH₃ plasma treatment was used to support the experimental results in the text. (a) and (c) are low-resolution TEM images of MoS₂ before and after processing, respectively. (b) and (d) are the corresponding high-resolution TEM images, respectively. (e) An electron image of a pristine MoS₂ flake. (f) EDS layered image, EDS mapping images of (g) S element and (h) Mo element of pristine sample. (i) EDS layered image, EDS mapping images of (j) S element, (k) Mo element and (l) N element of MoS₂ flake after treatment. The RF power is 20 W, and the processing time is 2 minutes.

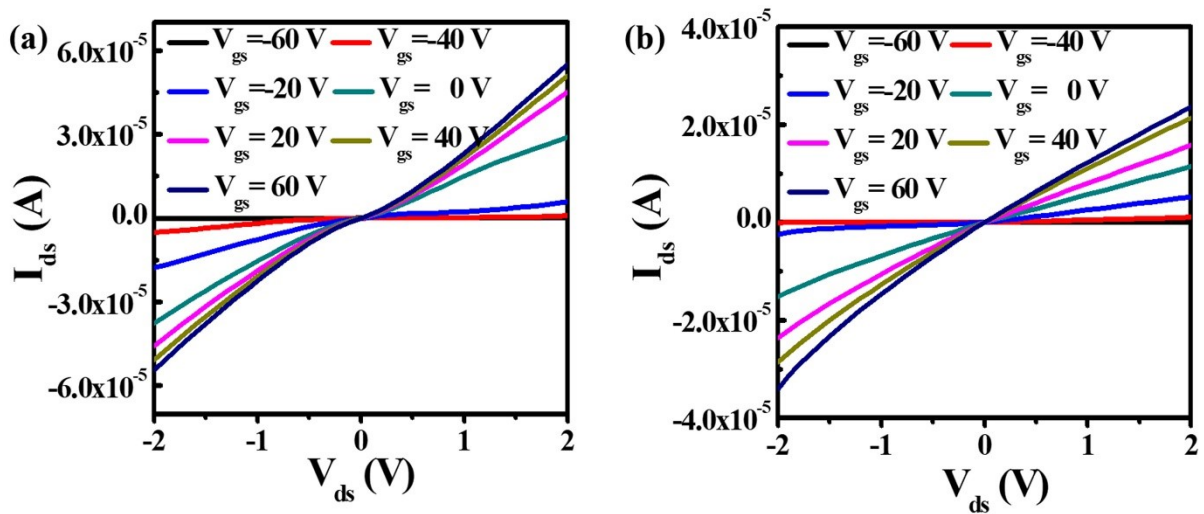


Figure S3 Output characteristics of (a) the pristine thin-layer MoS₂ FET device and (b) the device after NH₃ plasma treatment with 10 W radio frequency power for 2 minutes.

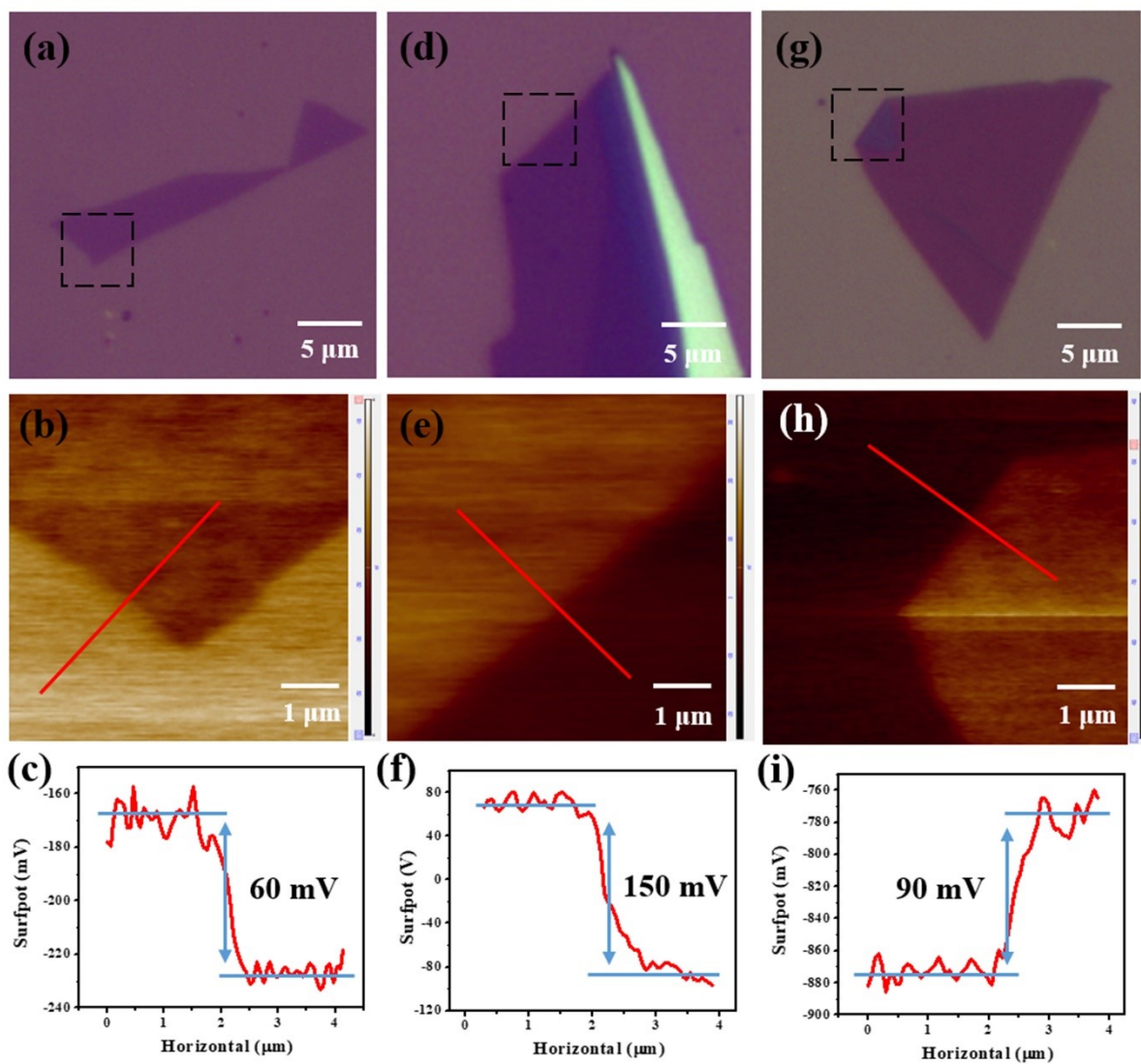


Figure S4 KPFM Characterizations of a pristine MoS₂ sample and two typical MoS₂ samples under 10 W, 1 min and 20 W, 2 mins treatment conditions. (a), (d) and (g) are the optical microscope images of pristine MoS₂ samples used in the experiment. The thickness of these samples are 3 nm. After that, the sample in (a) was not treated, the sample in (d) was treated with NH₃ plasma at 10 W for 1 minute, and the sample in (g) was treated with NH₃ plasma at 20 W for 2 minutes. (b), (e) and (h) correspond to the KPFM images of the black frame area in (a), (d) and (g) respectively. (c), (f) and (i) are the potential diagrams at the red lines in (b), (e), and (h) respectively.

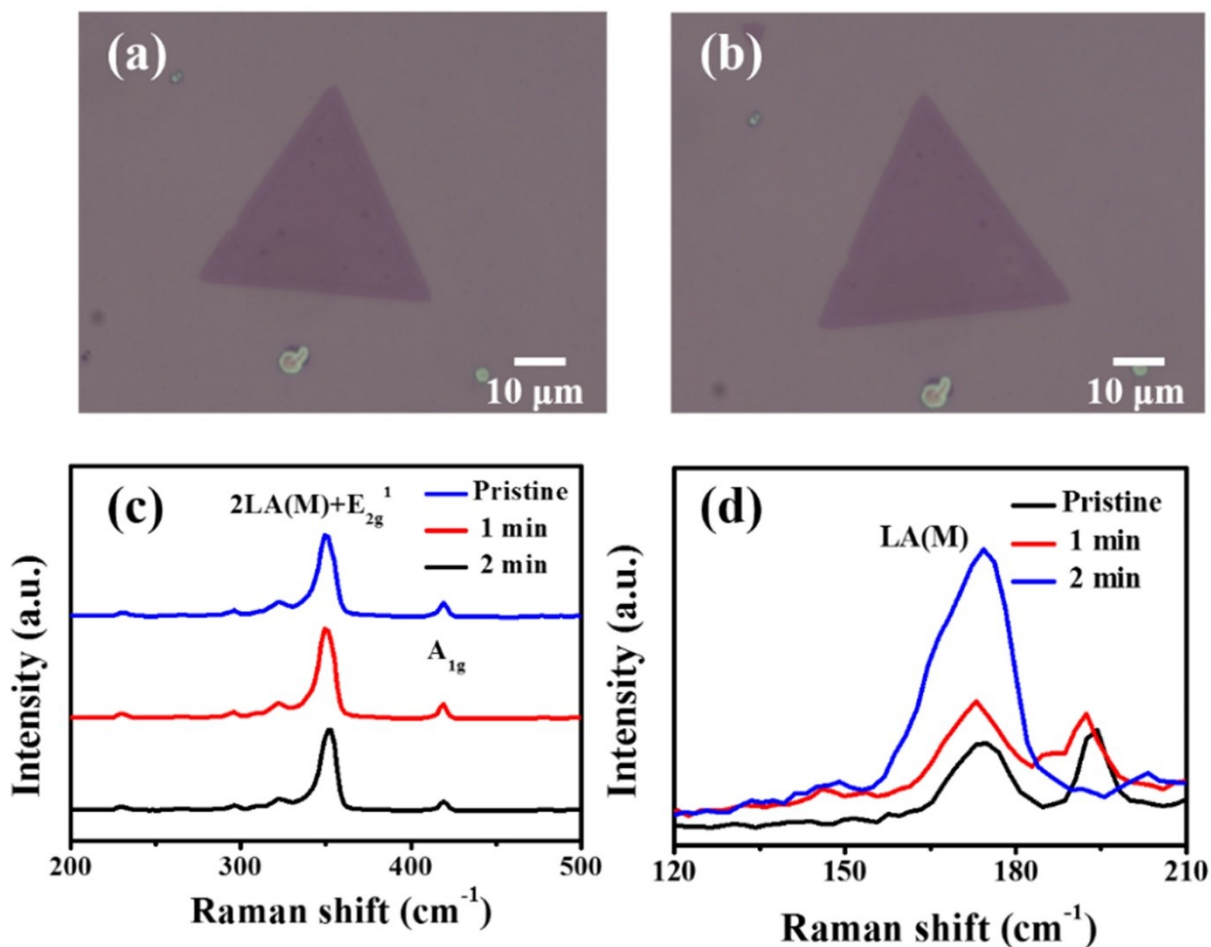


Figure S5 Optical microscope images of WS₂ monolayer grown by CVD (a) before and (b) after treatment (RF power = 10 W, time = 2 min). (c) Raman spectra of pristine and treated WS₂. (d) Enlarged image of LA(M) peak in (c). The increase in the intensity and area of the LA(M) peak indicates that as the processing time increases, the phonon scattering lifetime and the number of scattering centers increase, indicating that the doping process of the sample cannot be continued for too long to avoid causing too much crystal lattice damage on the sample.¹

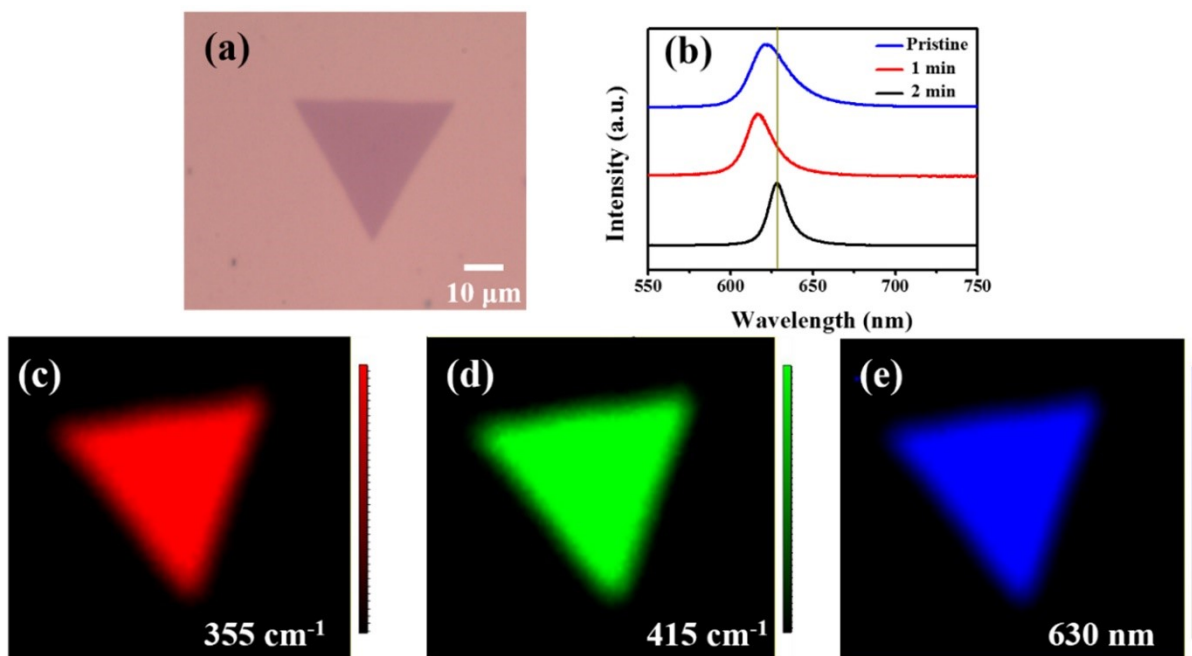


Figure S6 PL spectrums of WS₂ monolayer. (a) Optical microscope image of pristine WS₂ monolayer. (b) PL spectra of the pristine WS₂ and the samples processed at different times. Raman mapping images of (c) E_{2g}¹ peak (355 cm⁻¹) and (d) A_{1g} peak (415 cm⁻¹) of sample processed for 2 minutes. (e) PL mapping (630 nm) of sample processed for 2 minutes. The RF power used in this experiment is 10 W.

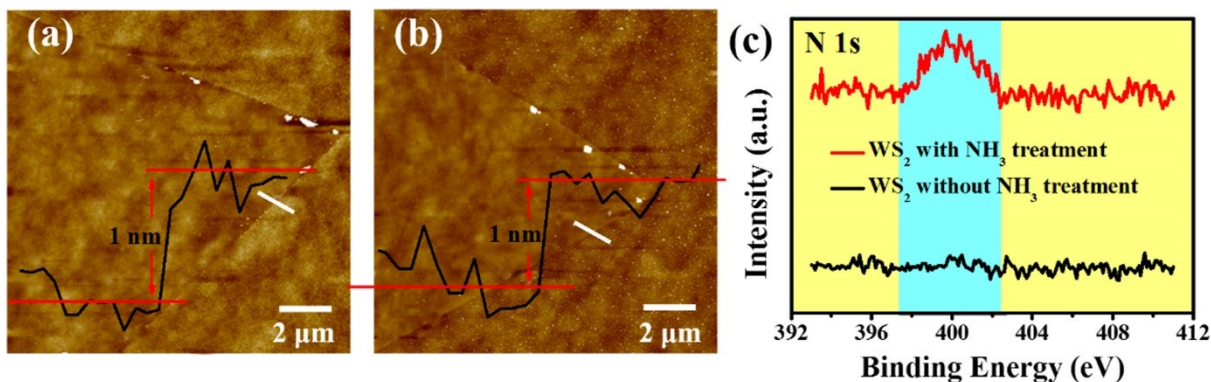


Figure S7 AFM images of WS₂ monolayer (a) before and (b) after NH₃ plasma processing. (c) The high-resolution N 1s XPS spectrum of pristine and treated WS₂. RF power = 10 W, time = 2 min.

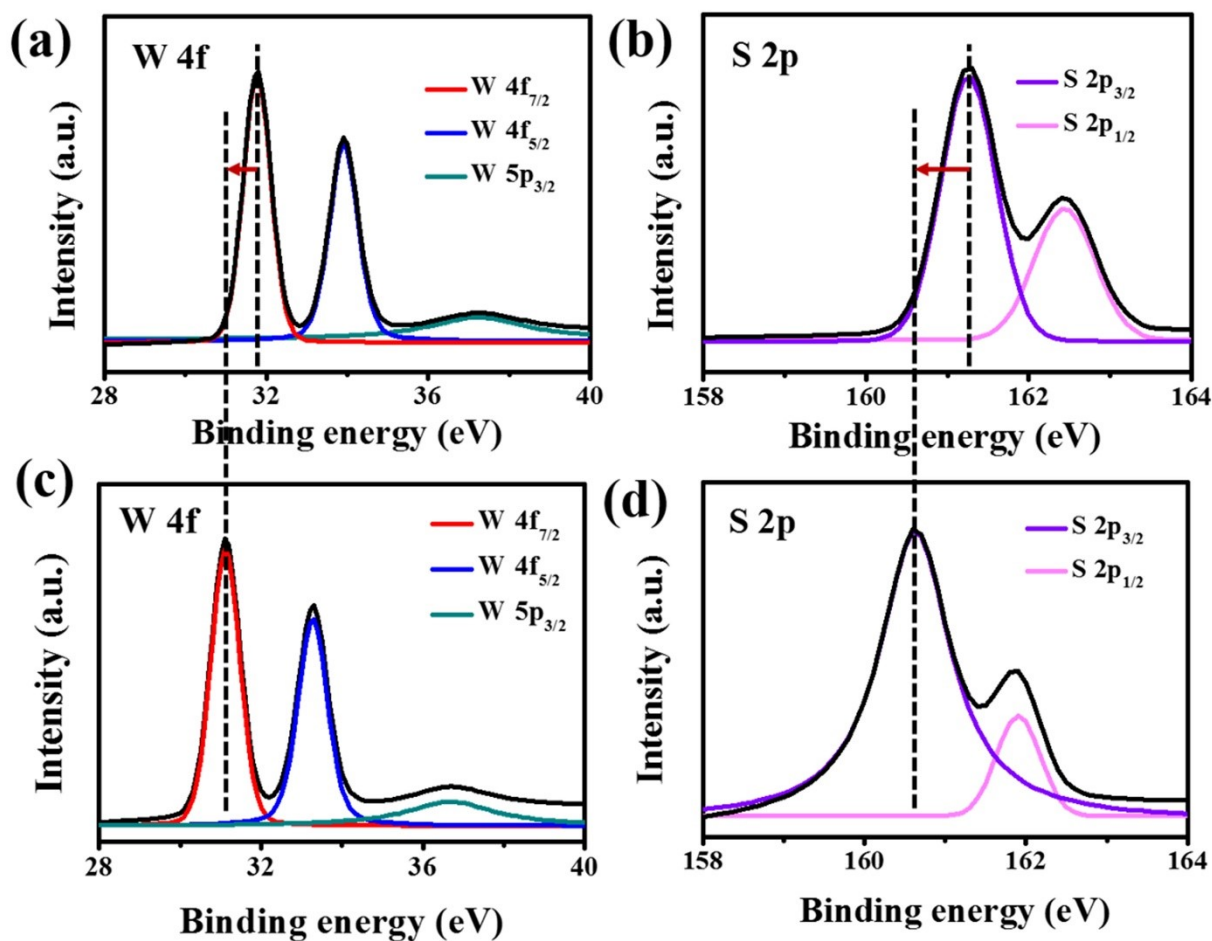


Figure S8 XPS spectrums of W 4f and S 2p (a)-(b) before and (c)-(d) after treatment of WS₂ monolayer. The W 4f peak is formed by the combination of W atoms and S atoms, and W 5p is caused by the residual Na₂WO₄ during the CVD growth process. The W 4f and S 2p peaks show obvious red shift after the treatment, which is due to the incorporation of N elements in the WS₂ monolayer crystal lattice. It can be seen that after the treatment of NH₃ plasma, there is the doping of N element in WS₂, and the band structure has changed at the same time as the doping. The red shift of the W 4f and S 2p peaks can be inferred that the sample has occurred p-type doping.²

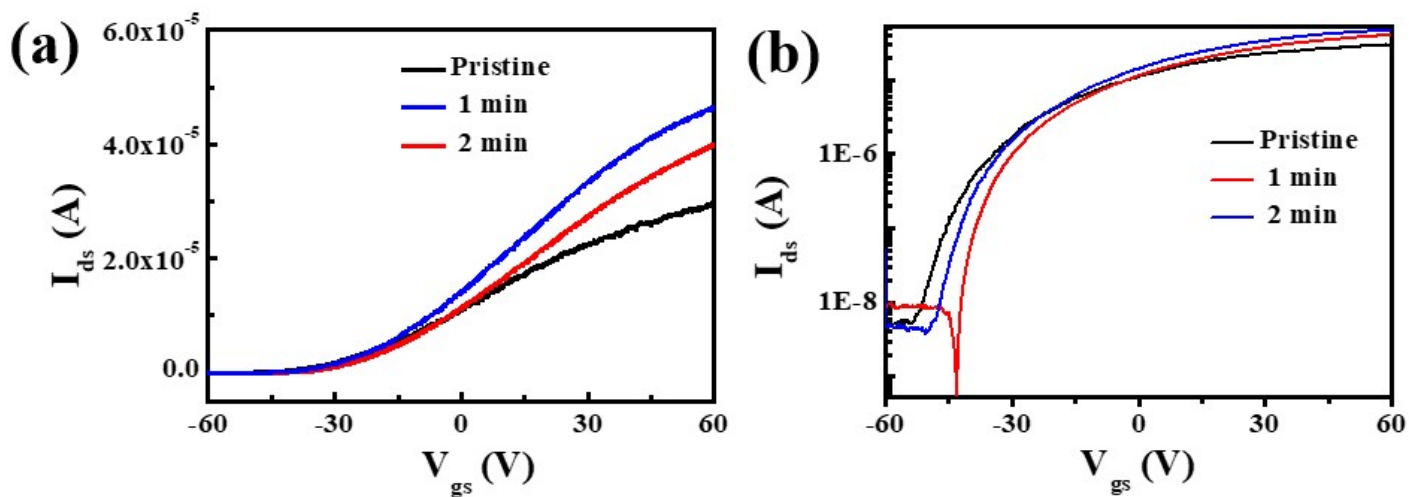


Figure S9 The (a) linear and (b) semi-logarithmic transfer characteristics of the WS₂ monolayer FET device, the RF power is 10 W. The threshold voltage has a significant positive shift, which indicates that p-type doping has occurred after the NH₃ plasma treatment. The initial V_{th} is -33.2 V, $V_{th} = -25.3$ V after 1 min treatment, $V_{th} = -27.8$ V after 2 min treatment. This shows that when the RF power is low and the treatment time is relatively short, the N element fills the S vacancies in the WS₂ monolayer, reduces lattice scattering and increases the carrier mobility, and the sample is p-type doped. As the processing time increases, the surface produces many S vacancies due to the etching effect of H radicals, which is greater than the p-type effect caused by N element doping, and then n-type doping occurs.

References

1. J. K. Li, W. T. Su, F. Chen, L. Fu, S. Ding, K. X. Song, X. W. Huang and L. J. Zhang, *J. Phys. Chem. C*, 2019, **6**, 3900-3907.
2. G. Meisl, K. Schmid, O. Encke, T. Hoeschen, L. Gao and C. Linsmeier, *New J. Phys.*, 2014, **16**, 093018.