

Defect-Engineered Monolayer MoS₂ with Enhanced Memristive and Synaptic Functionality for Neuromorphic Computing

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Supplementary Information

XPS characterization of pristine MoS₂

Figure S1a and S1b represents the XPS of MoS₂, The Mo 3d (figure S1a) spectra exhibit two prominent peaks at ~ 229.87 eV and ~ 233 eV, corresponding to the Mo 3d_{5/2} and Mo 3d_{3/2} states, respectively. These peaks align with the reported binding energies for MoS₂, confirming the presence of molybdenum in its characteristic oxidation states.¹ Additionally,

a peak is observed at ~ 227 eV, corresponding to the S 2s state. However, another peak was observed at approximately 236 eV, which can be attributed to MoO_3 ² or MoO_x suboxide species.³

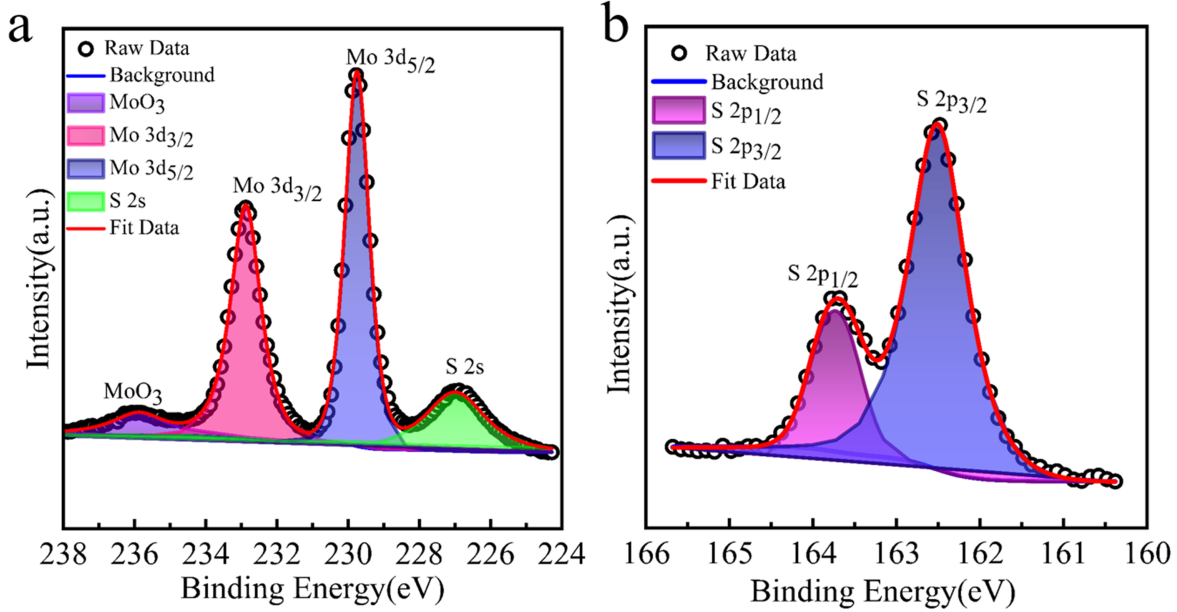


Figure S1: X-ray Photoelectron spectra (XPS) of CVD-grown MoS_2 (a) XPS of Mo 3d core level for CVD-grown MoS_2 flakes on SiO_2/Si (b) XPS spectra of S 2s core level.

This peak indicates the presence of nonstoichiometric MoS_2 , likely resulting from incomplete sulfurization of MoO_3 or MoO_x suboxides. This observation has been previously reported in CVD-grown MoS_2 samples.¹ However, it is important to note that the intensity of this peak is significantly lower compared to the $\text{Mo 3d}_{5/2}$ and $\text{Mo 3d}_{3/2}$ peaks, suggesting that the amount of oxide present in our CVD-grown sample is minimal. Figure S1b presents the S 2p spectra, revealing two distinct peaks observed at ~ 163.7 eV and ~ 162.5 eV, corresponding to the S 2p_{1/2} and S 2p_{3/2} states, respectively.

Atomic Force Microscopy

Figure S2a shows the AFM image of CVD-grown MoS₂, and Figure S2b shows the corresponding height profile revealing the thickness of as-grown MoS₂ is 0.65 nm.

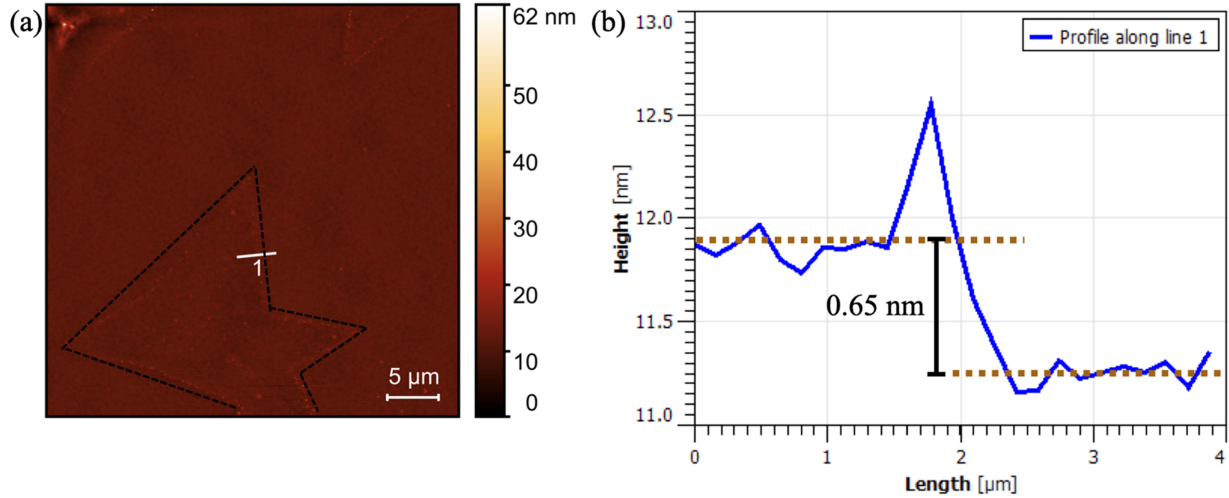


Figure S2: (a) AFM image of CVD-grown MoS₂ (b) Height profile along the white line shown in a showing the thickness of CVD-grown MoS₂.

Optical image of fabricated device

Figure S3a is the optical micrograph of CVD-grown MoS₂ showing the coverage and quality of the monolayer. Figure S3b represents the optical micrograph of the fabricated device.

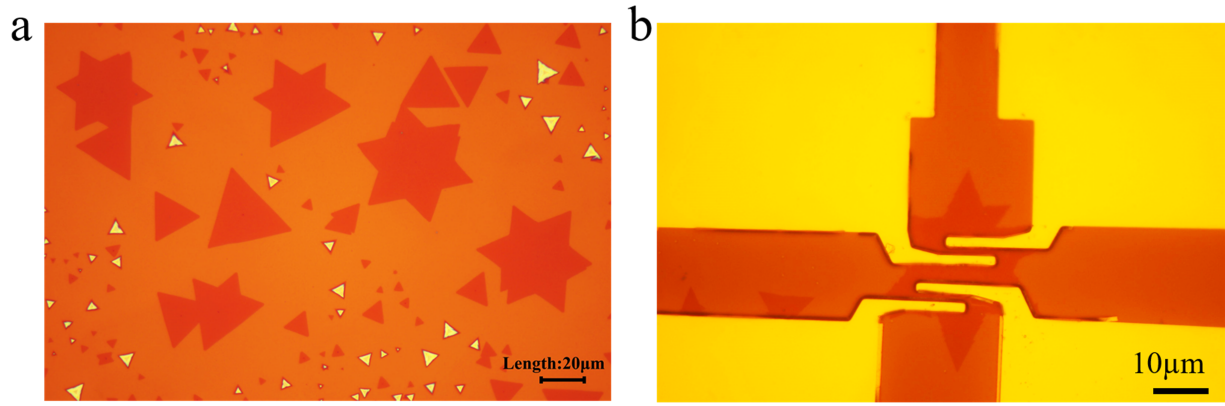


Figure S3: Optical micrograph of CVD-grown MoS₂ and fabricated device. (a) Optical micrograph of CVD-grown MoS₂. (b) Optical micrograph of the fabricated device on CVD-grown MoS₂.

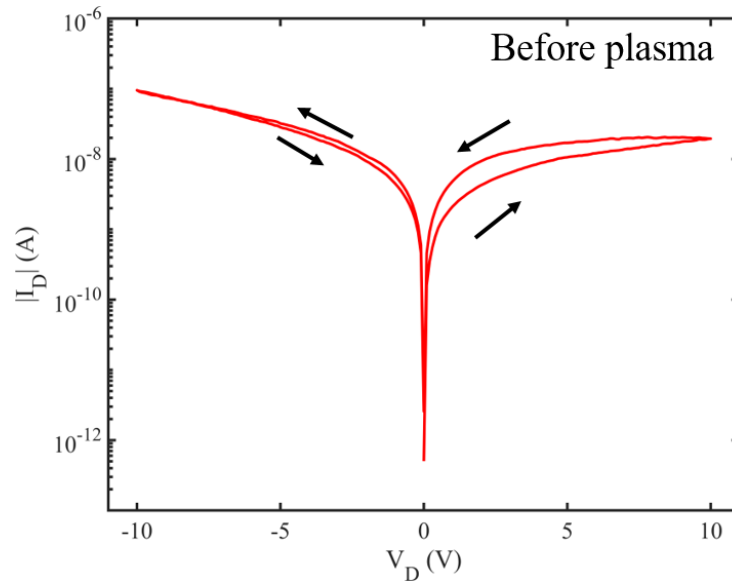


Figure S4: Log scale graph of figure 3a in the main text

Ar Plasma Impact at Various Power Levels

Raman PL and XPS characterization of low power Ar plasma treated sample

Figure S5 shows the Raman and PL spectra before and after low-power Ar plasma treatment. The peak position and FWHM of peaks in Raman spectra do not change after low-power plasma treatment. Additionally, the B/A intensity ratio in PL, which indicates the defect density in the sample,⁴ does not change after low-power plasma treatment.

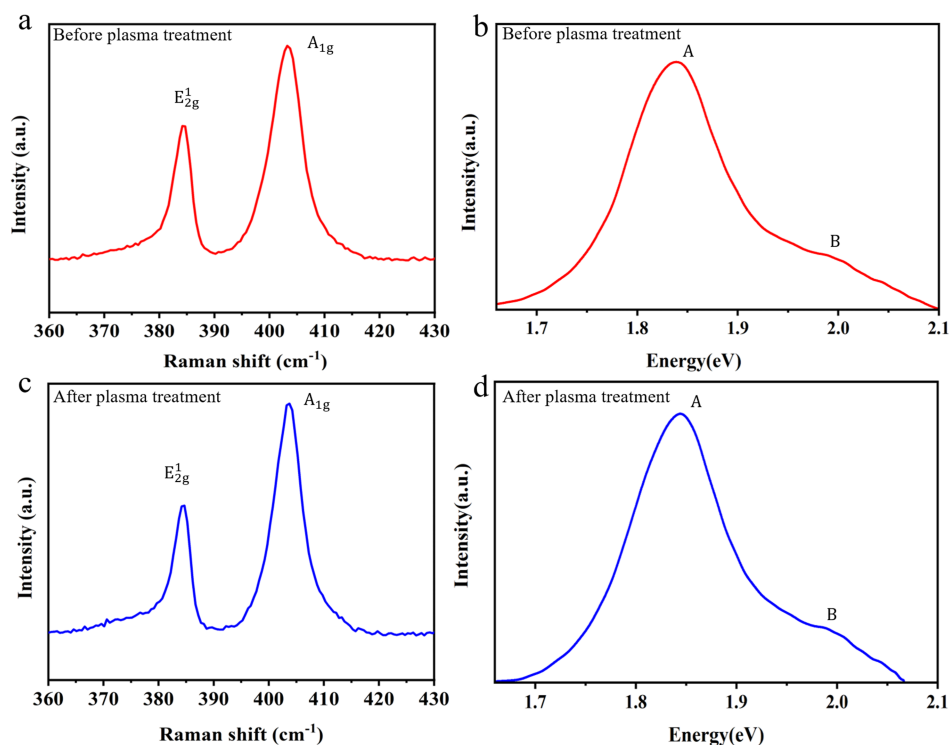


Figure S5: Raman and PL spectra before and after low power plasma treatment. (a) Raman spectra before plasma treatment. (b) PL spectra before plasma treatment (c) Raman spectra after low-power plasma treatment. (d) PL spectra after low-power plasma treatment.

Figure S6 shows the XPS before and after low-power plasma; there is no shift in the binding energy and FWHM of peaks before and after low-power plasma treatment. So Raman, PL and XPS results verify that low-power plasma does not introduce sulfur vacancies in the

sample.

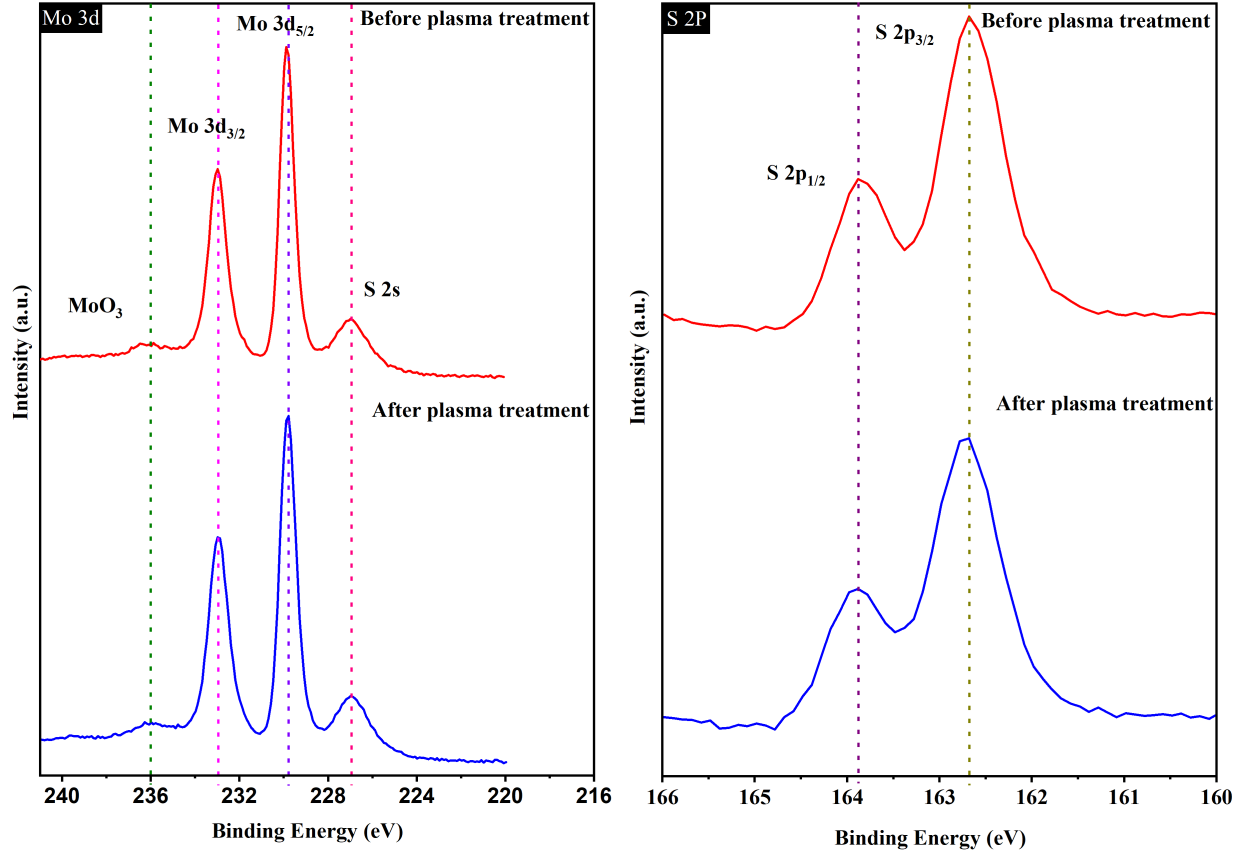


Figure S6: XPS of 3d and S 2p core level before and after low power plasma treatment

Raman and XPS characterization of optimal-power Ar plasma treated sample

Figure S7 presents the XPS spectra before and after optimal-power plasma treatment. Shift in the Mo 3d and S 2S peak to lower binding energy and increased FWHM reflects the introduction of sulfur vacancies in the sample.^{1,5,6} Figure S8 shows the fitted Raman spectra after optimal-power plasma treatment. Two new peaks arises at $\sim 377 \text{ cm}^{-1}$ and $\sim 411 \text{ cm}^{-1}$ which are attributed as disorder-induced peaks.⁷

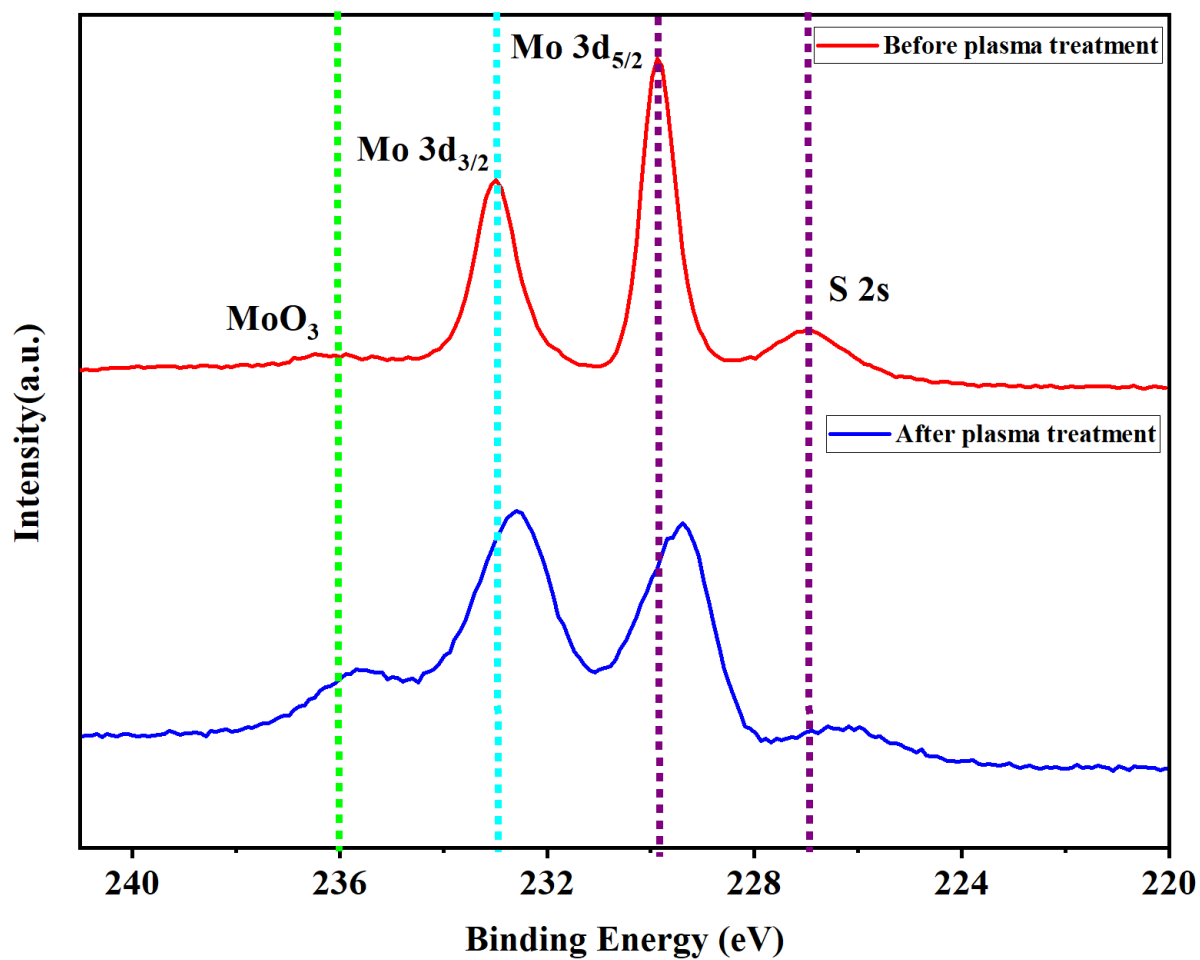


Figure S7: XPS spectra before and after optimal-power plasma treatment

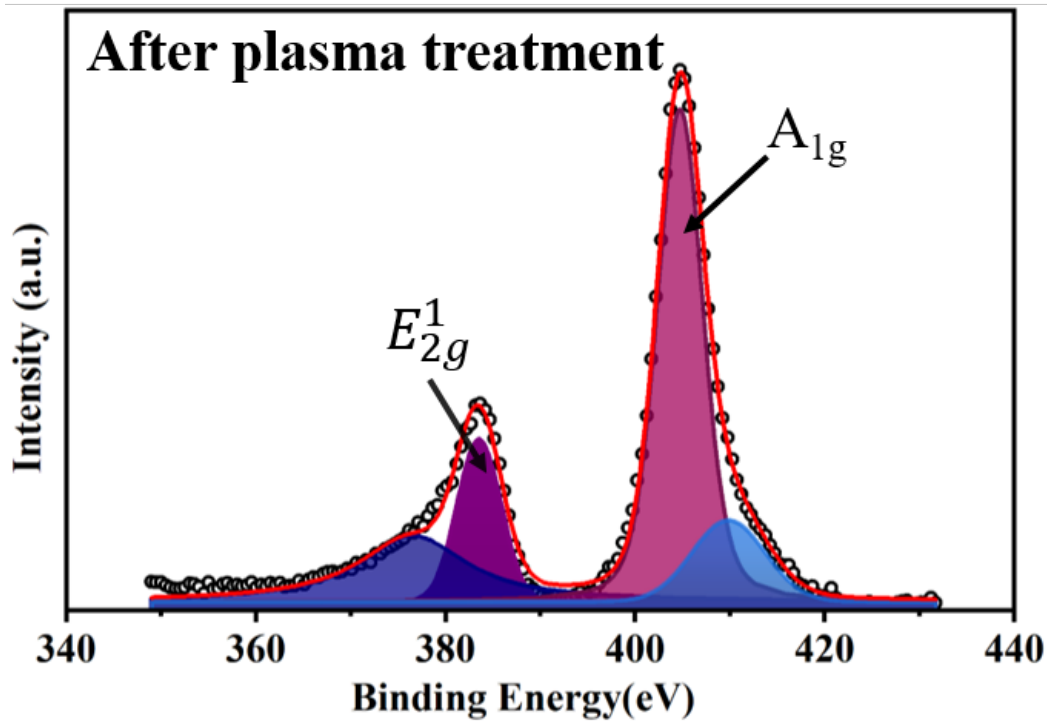


Figure S8: Fitted Raman spectra after optimal-power plasma treatment

Figure S9 is the optical image of optimal-power plasma treated MoS₂ for different time duration. Figure S10 shows the HAADF-STEM image of optimal-power plasma treated MoS₂, and arrows show the sulfur vacancies.

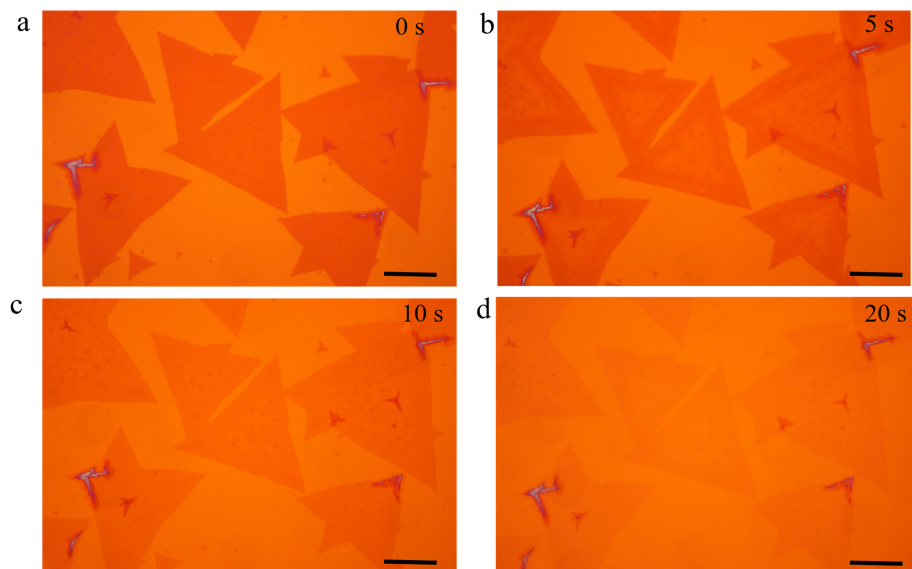


Figure S9: optical image of MoS₂ (a) before plasma treatment (b) after 5 seconds plasma treatment (c) after 10 seconds plasma treatment (d) after 20 seconds plasma treatment, scale bar of all images is 20 μm

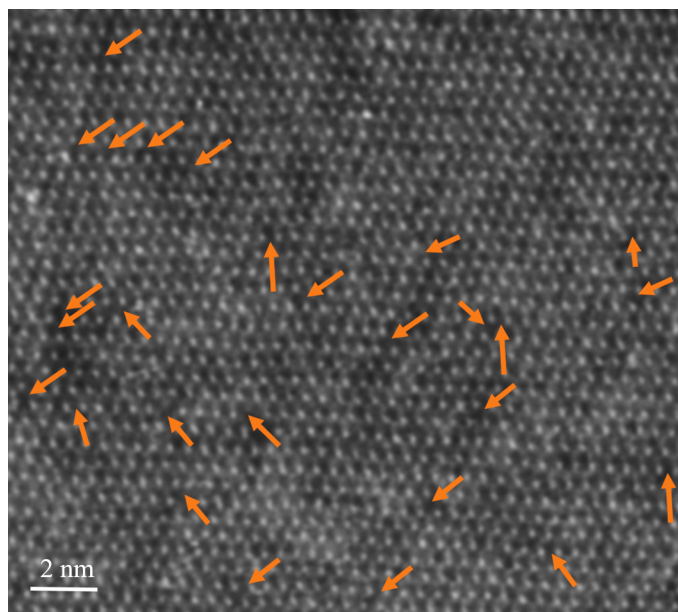


Figure S10: HAADF-STEM image of optimal-power plasma treated MoS₂

Raman and PL of high power Ar plasma treated sample

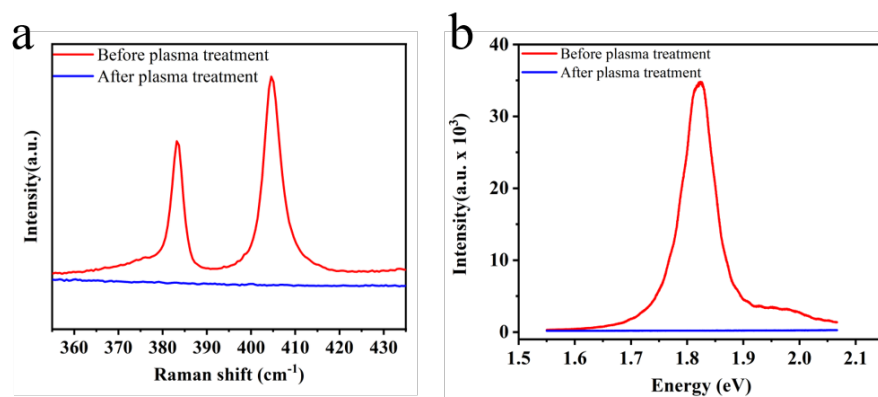


Figure S11: (a) Raman spectra before and after high power Ar plasma treatment (b) PL spectra before and after high power Ar plasma treatment

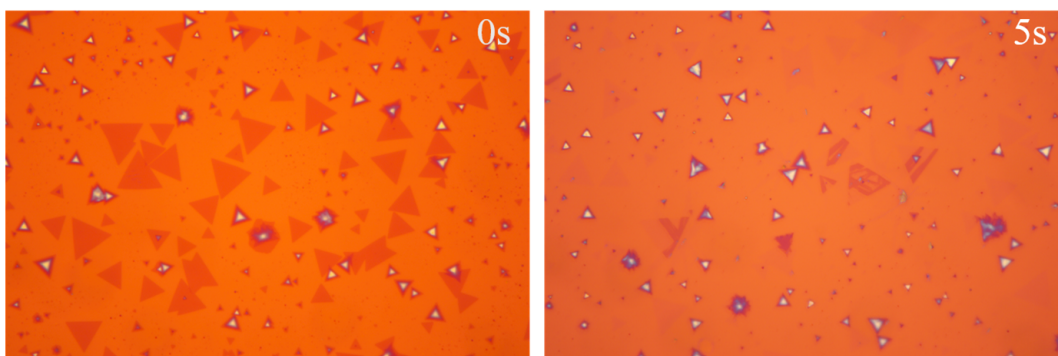


Figure S12: optical image of MoS₂ before and after high power plasma treatment

Electrical transport measurement of optimal-power plasma treated sample

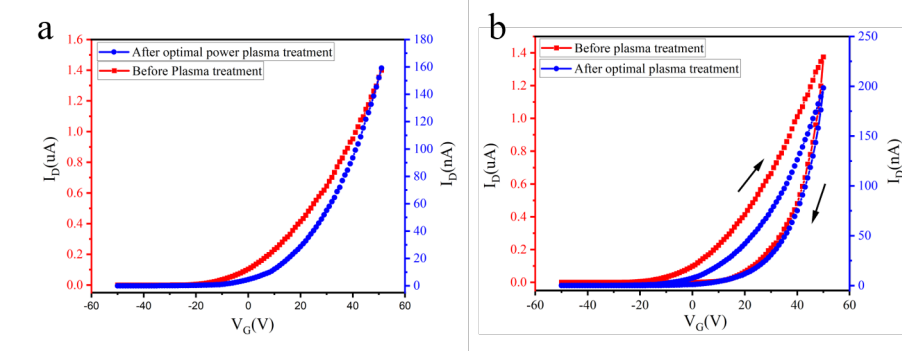


Figure S13: (a) Transfer characteristics (I_D versus V_G) of the device at V_D at 0.5 V, before plasma treatment in red colour and after optimal-power plasma treatment in blue colour (b) Hysteresis in transfer characteristics, I_D versus V_G at $V_D = 0.5$ V, black arrows show the sweeping direction.

Memristive and synaptic functionality before and after optimal-power plasma treatment

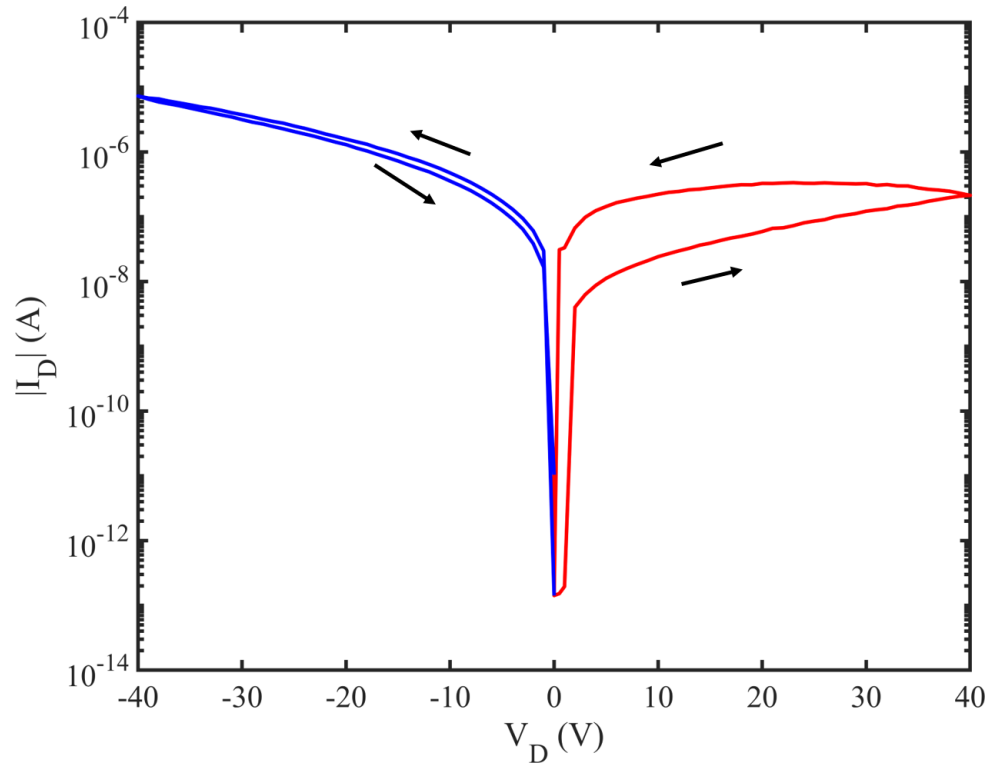


Figure S14: Log scale graph of figure 6a in the main text

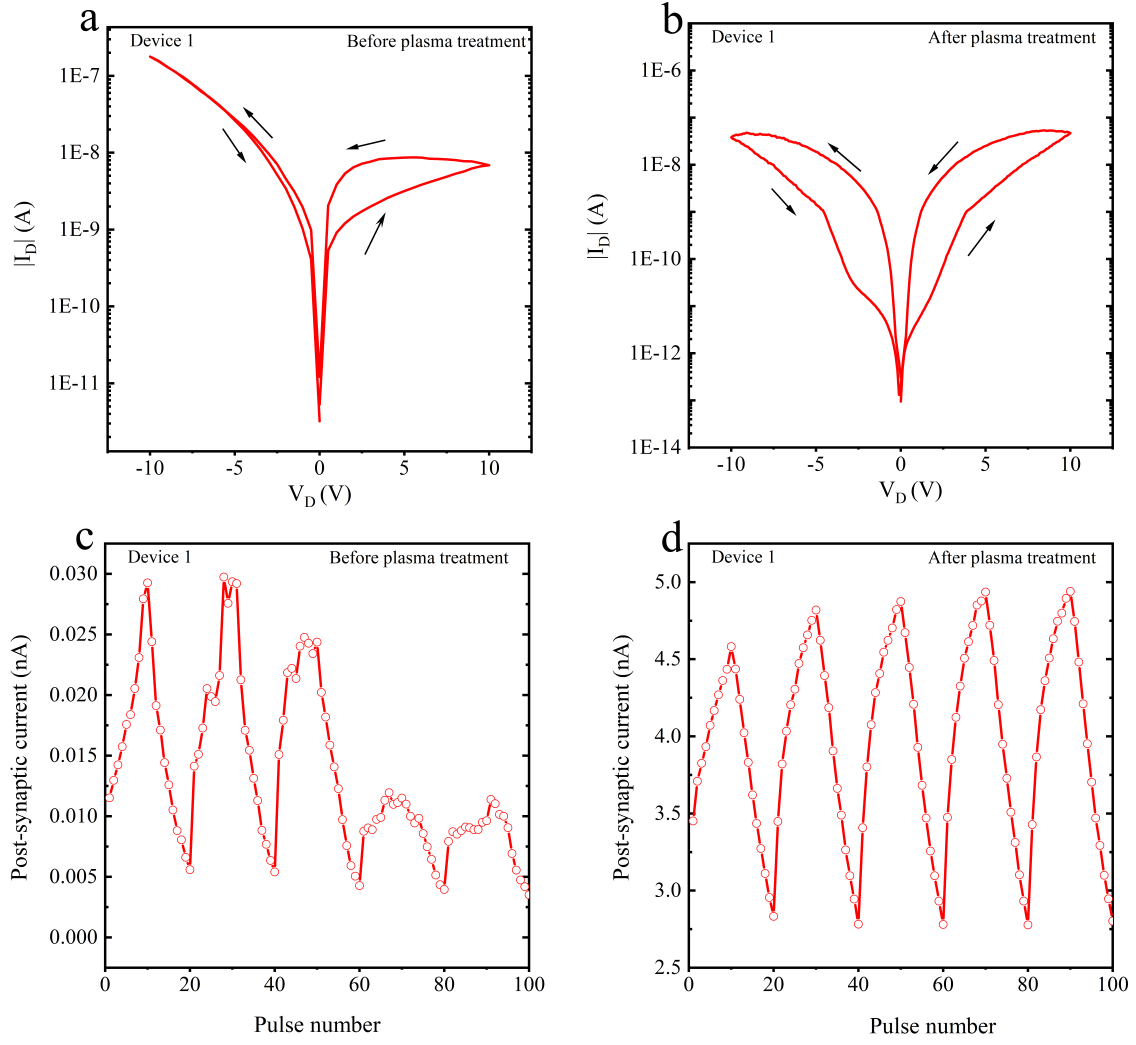


Figure S15: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

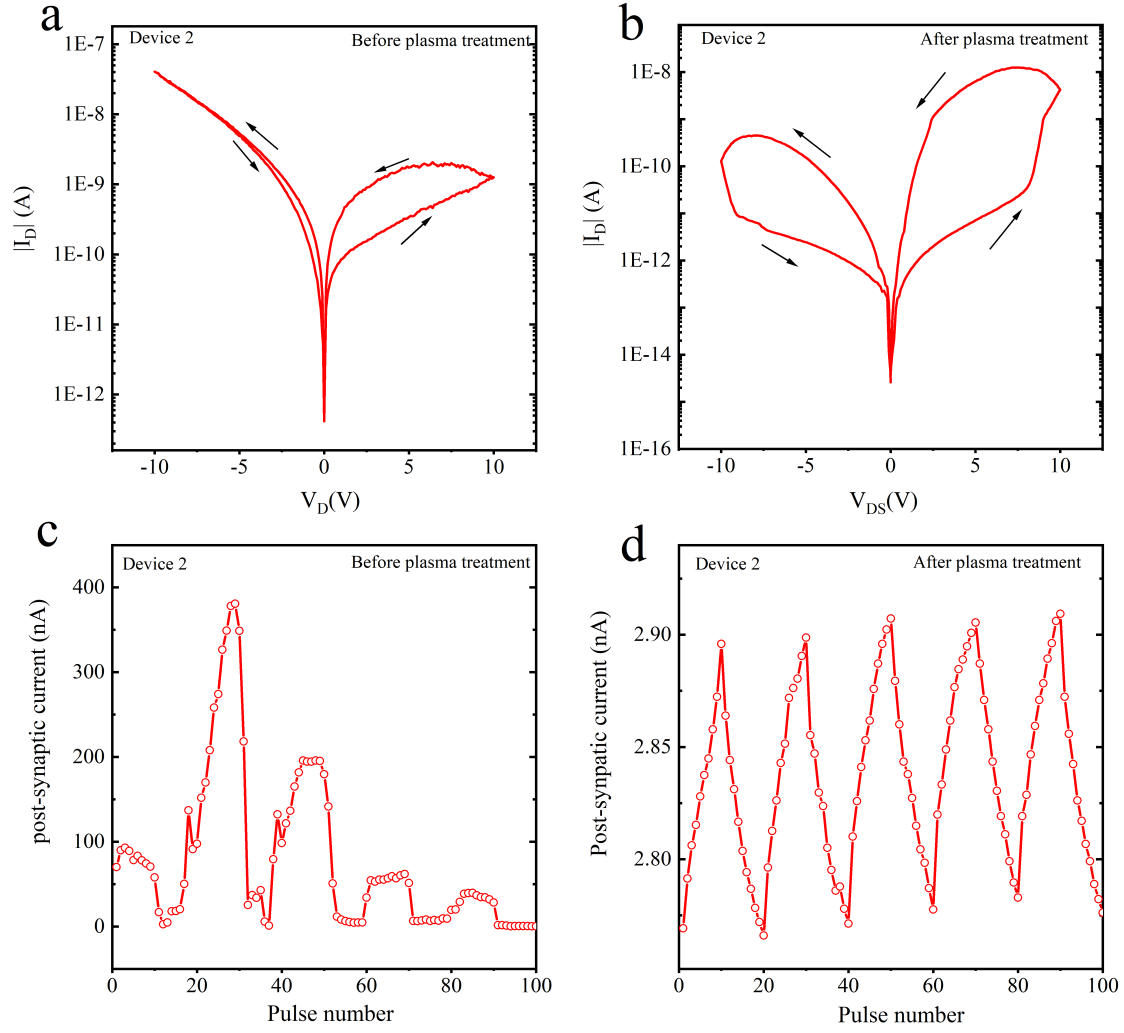


Figure S16: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

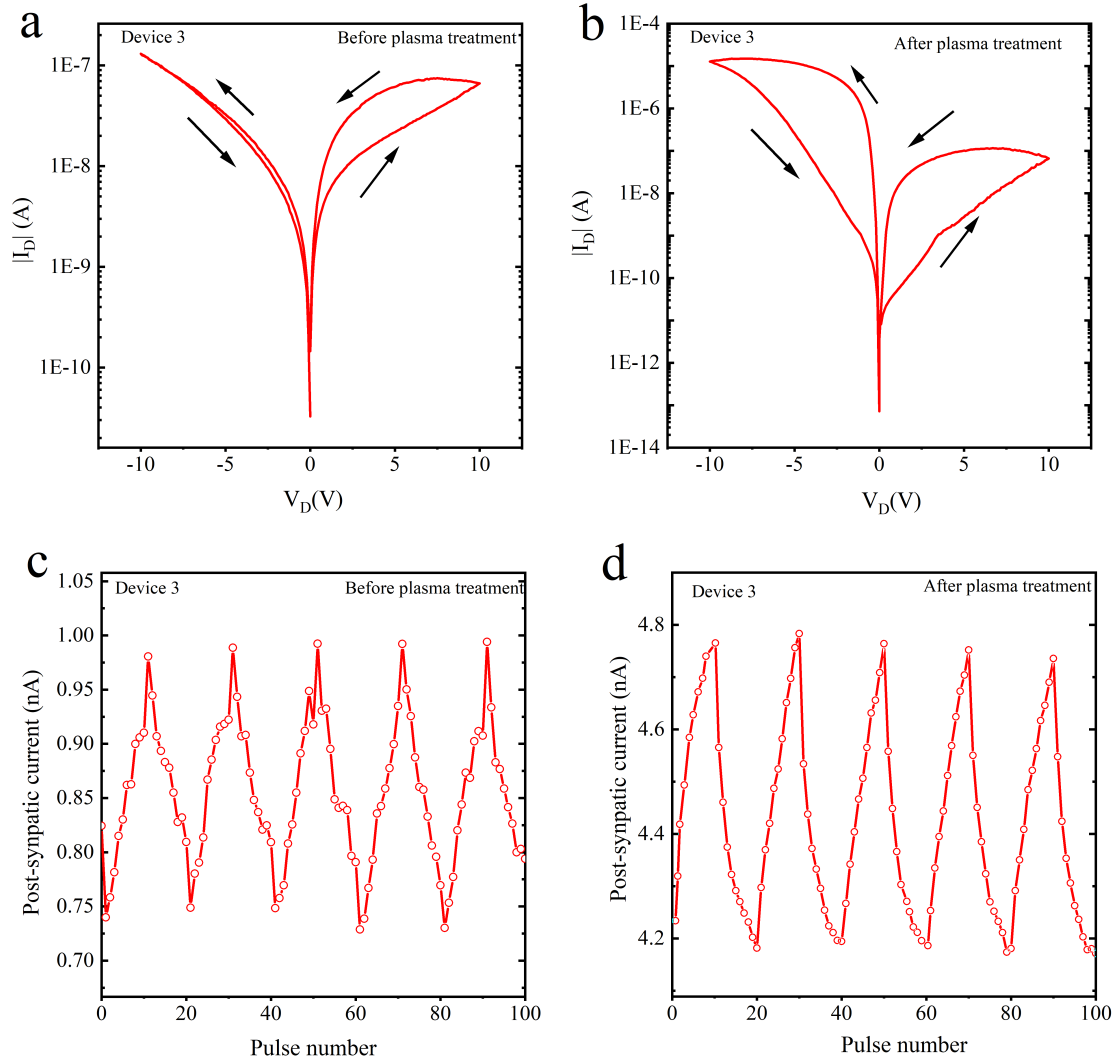


Figure S17: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment.

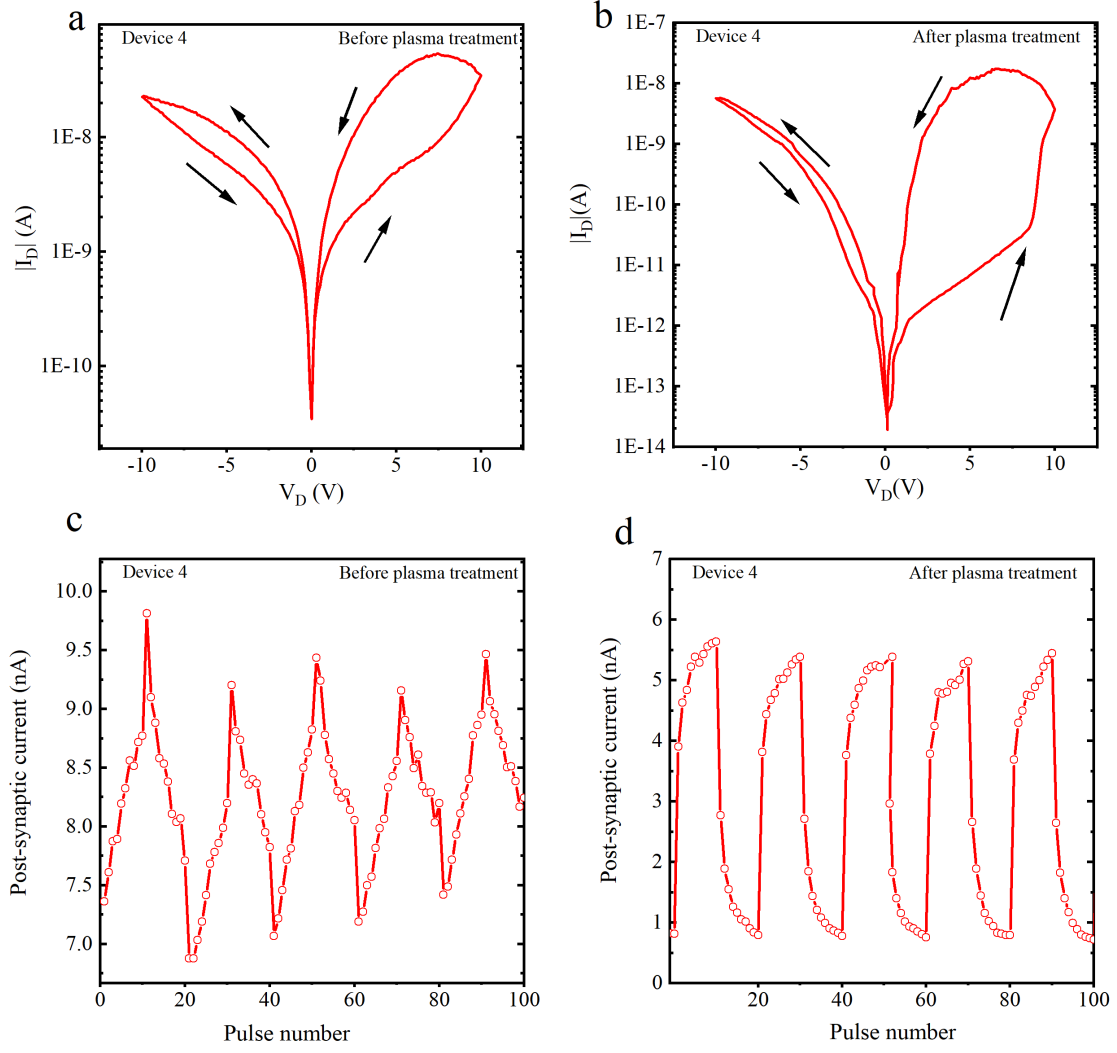


Figure S18: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

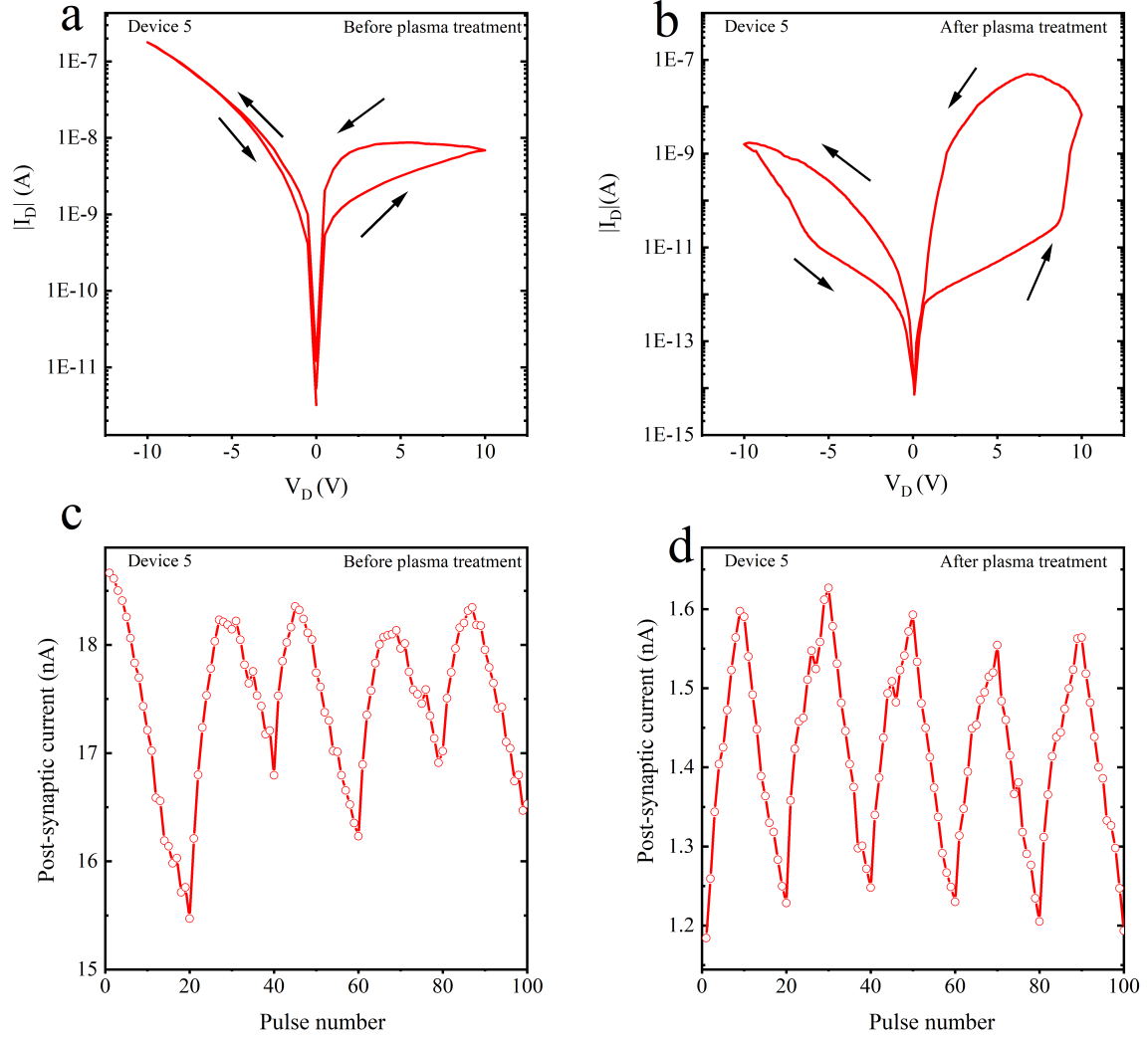


Figure S19: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

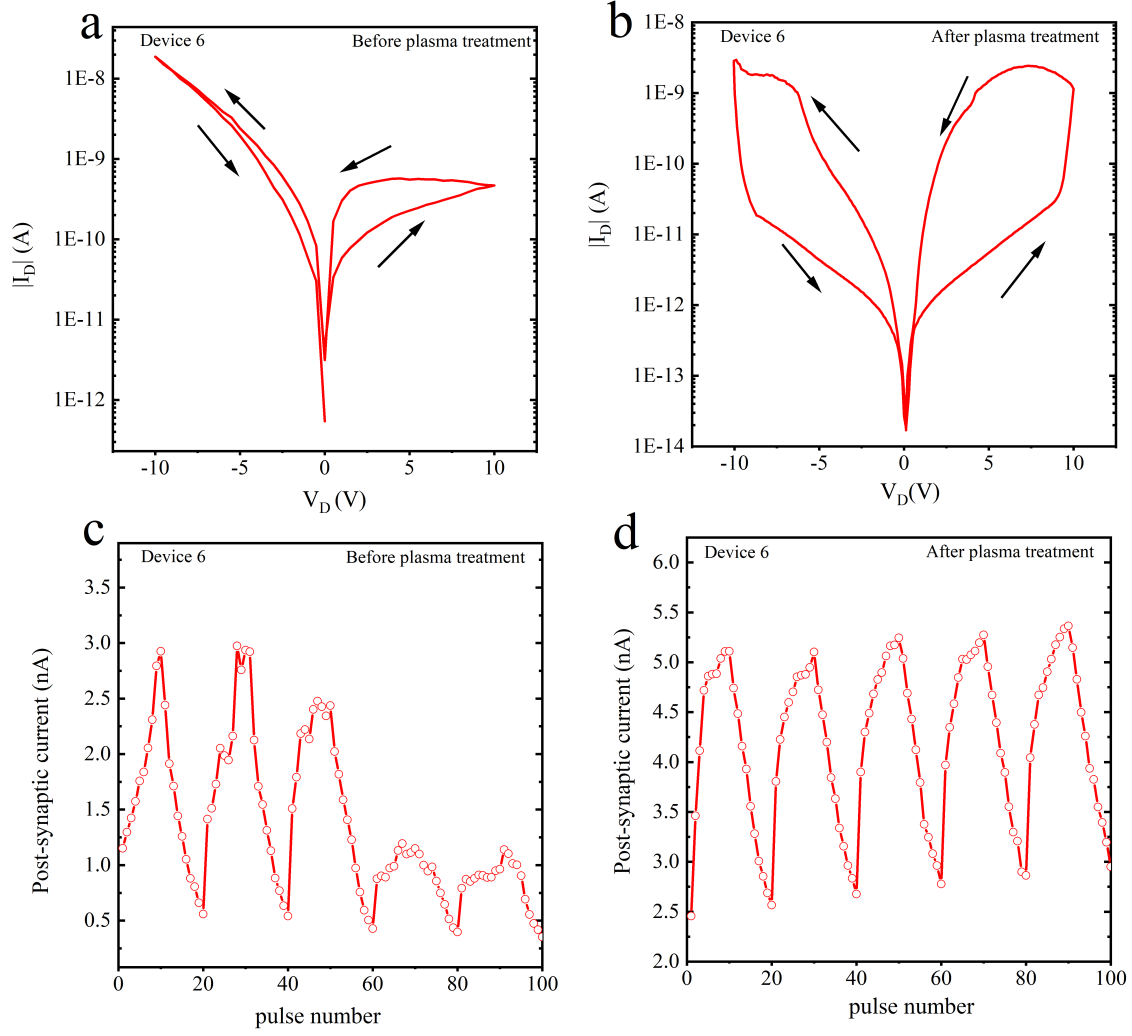


Figure S20: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

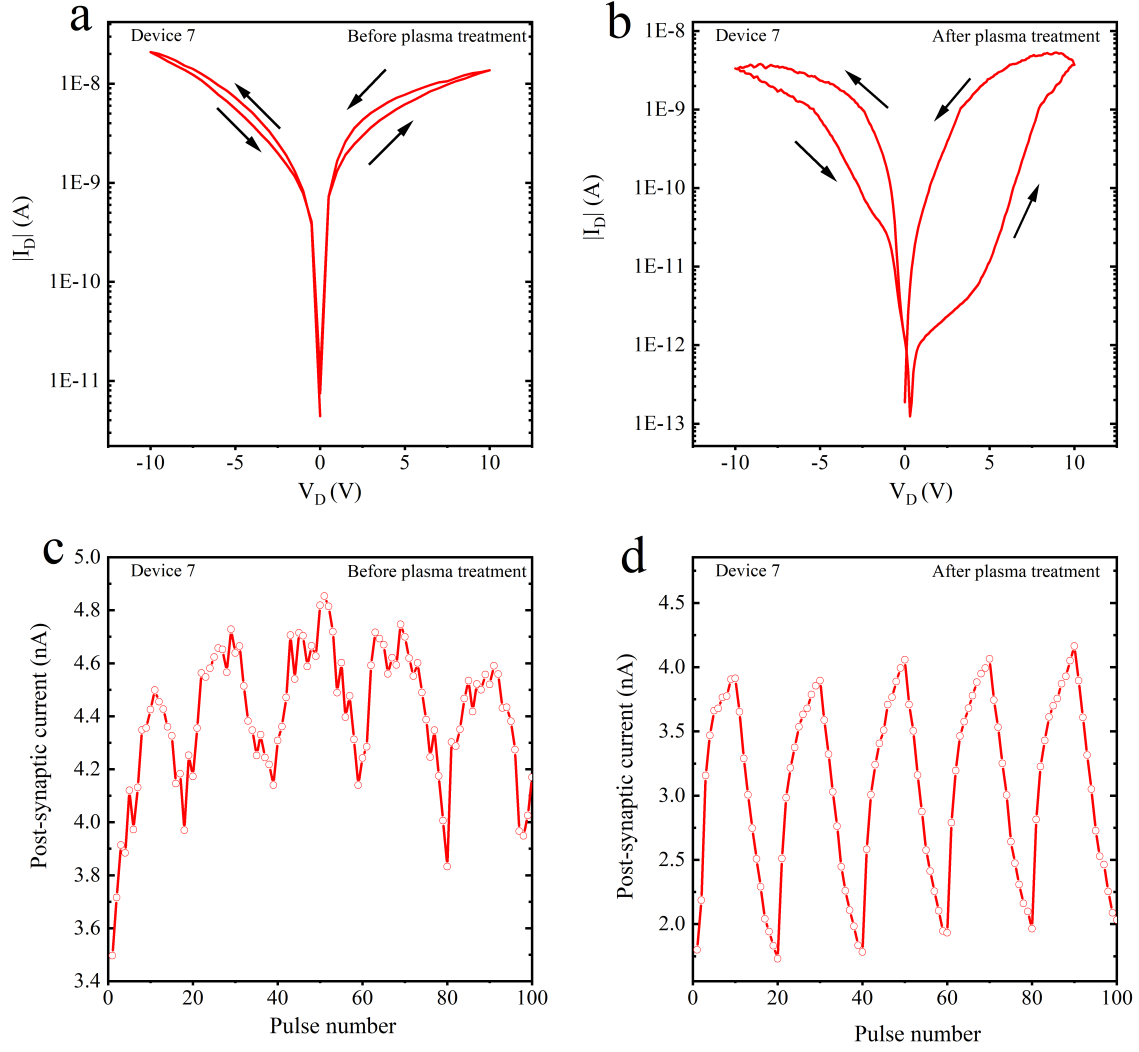


Figure S21: (a) I_D-V_D before plasma treatment (b) I_D-V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

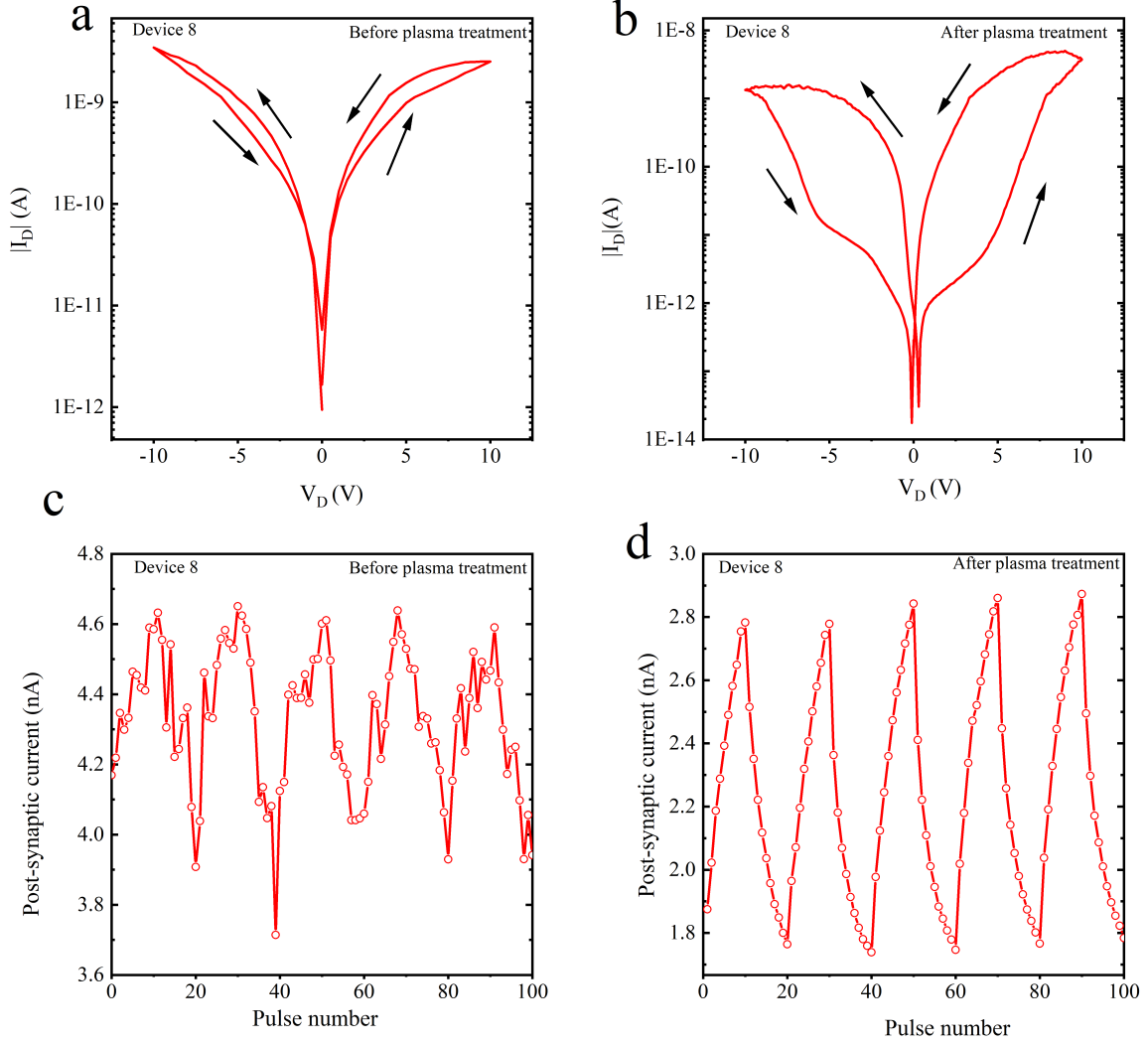


Figure S22: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

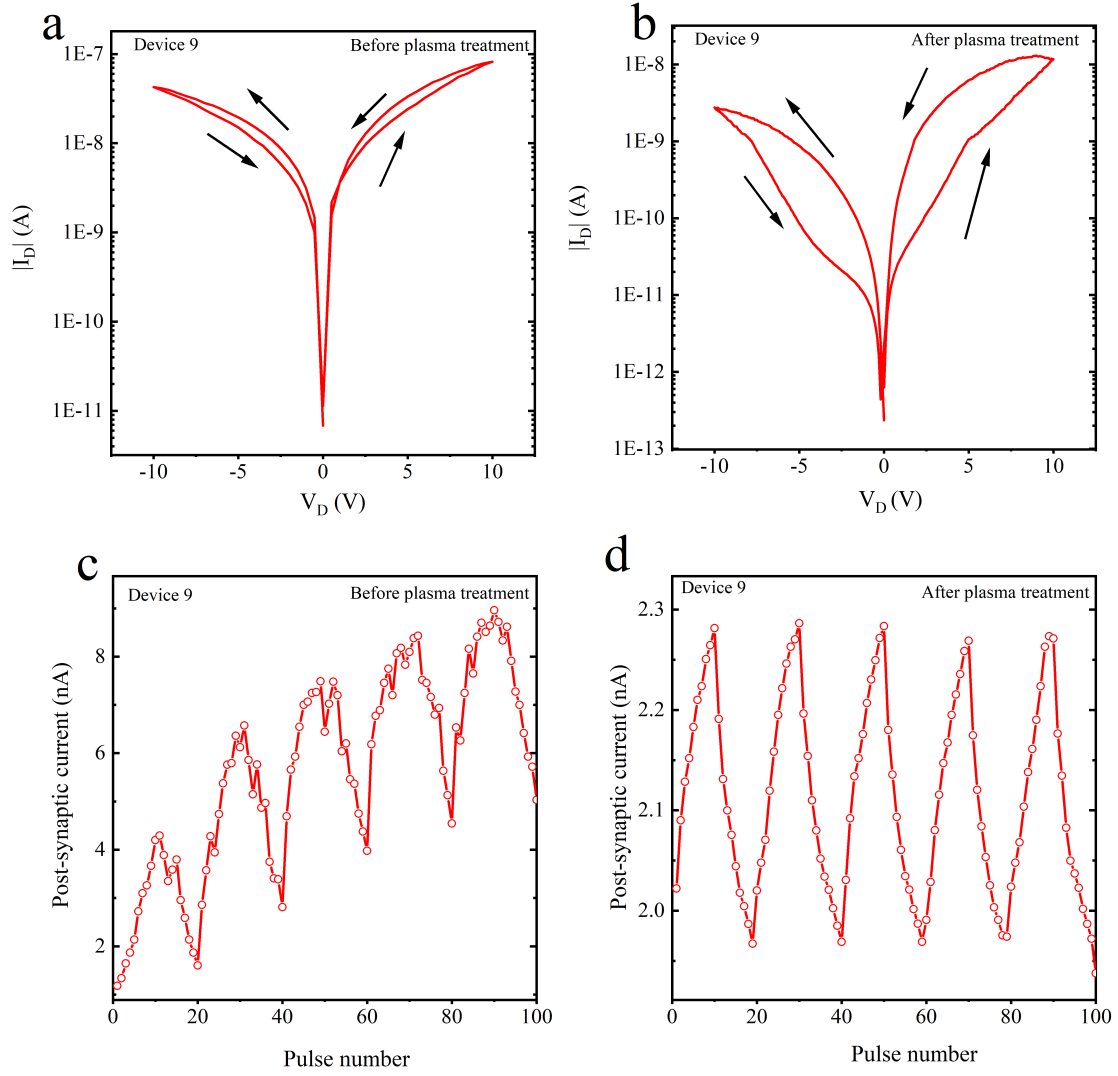


Figure S23: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

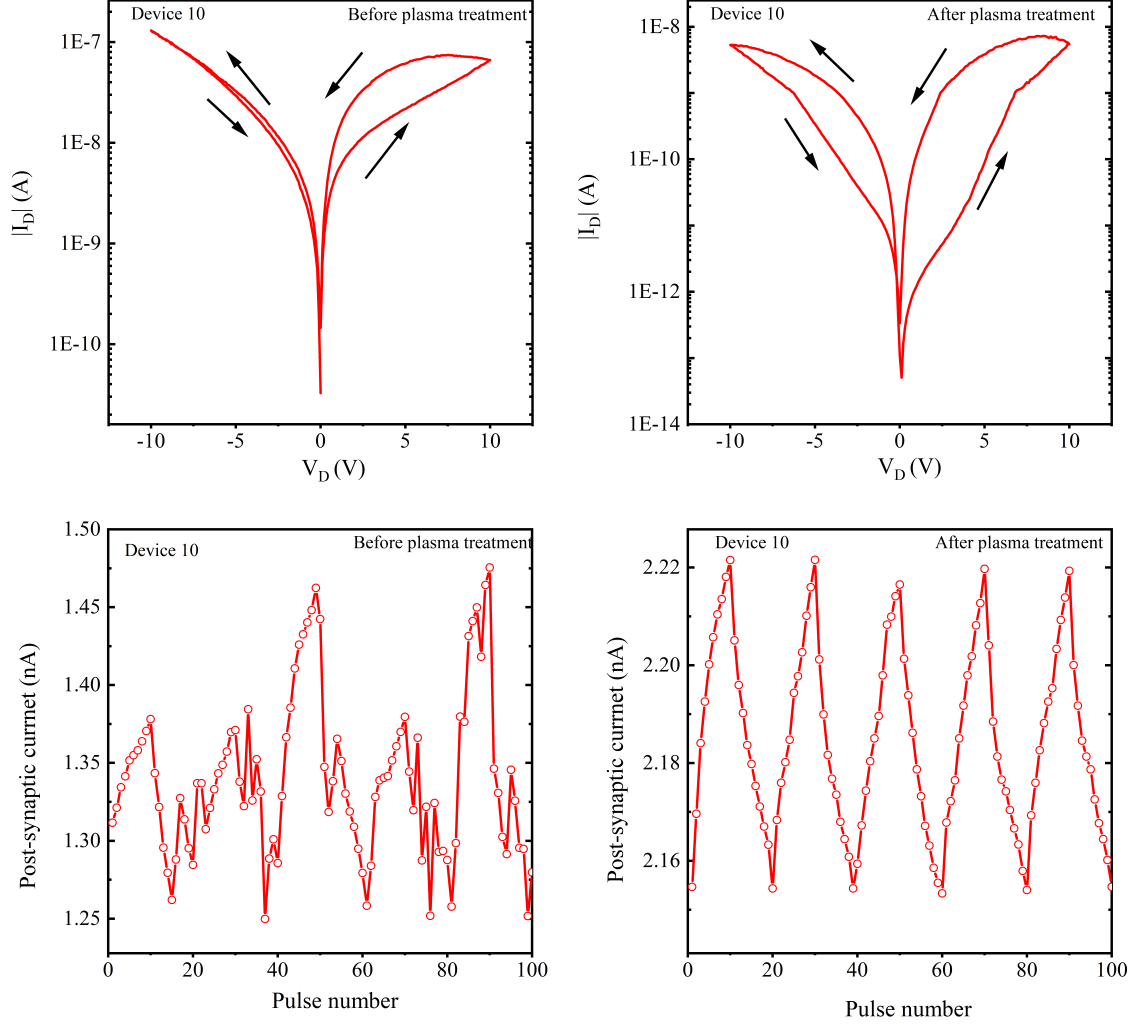


Figure S24: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment (c) LTP-LTD characteristics before plasma treatment (d) LTP-LTD characteristics after plasma treatment .

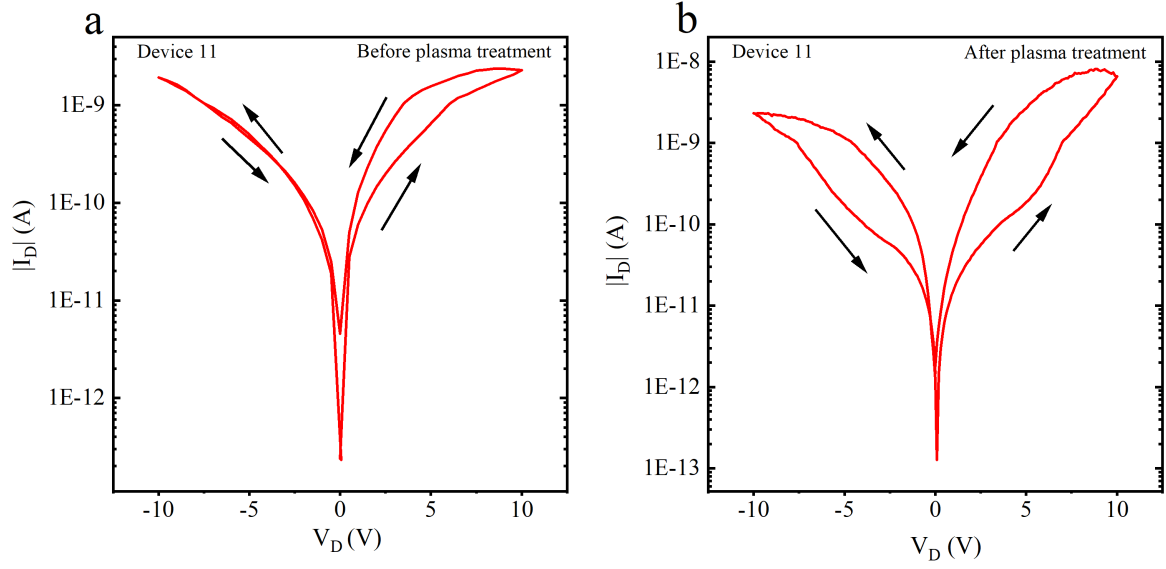


Figure S25: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment

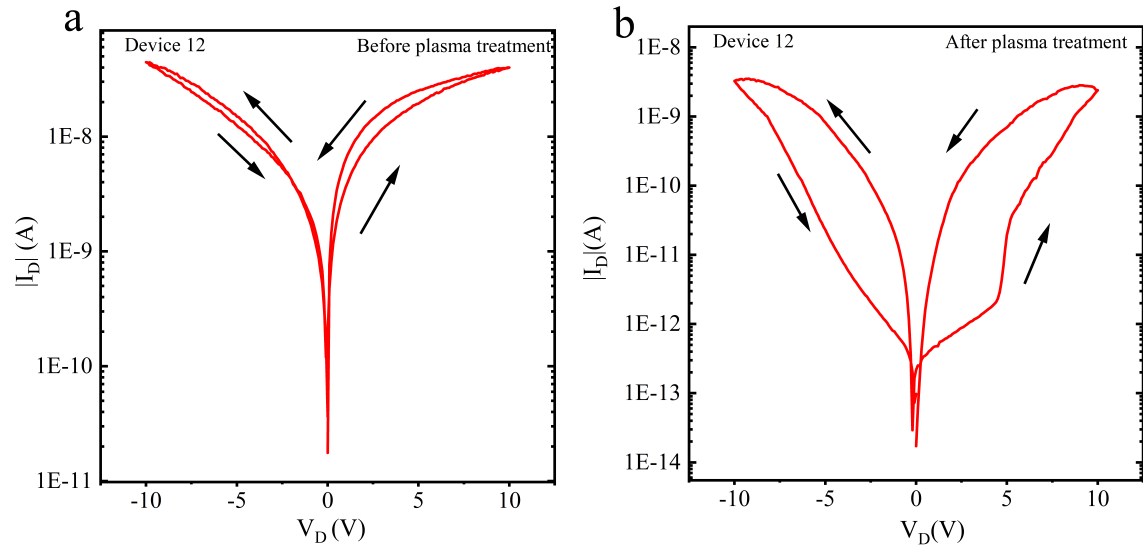


Figure S26: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

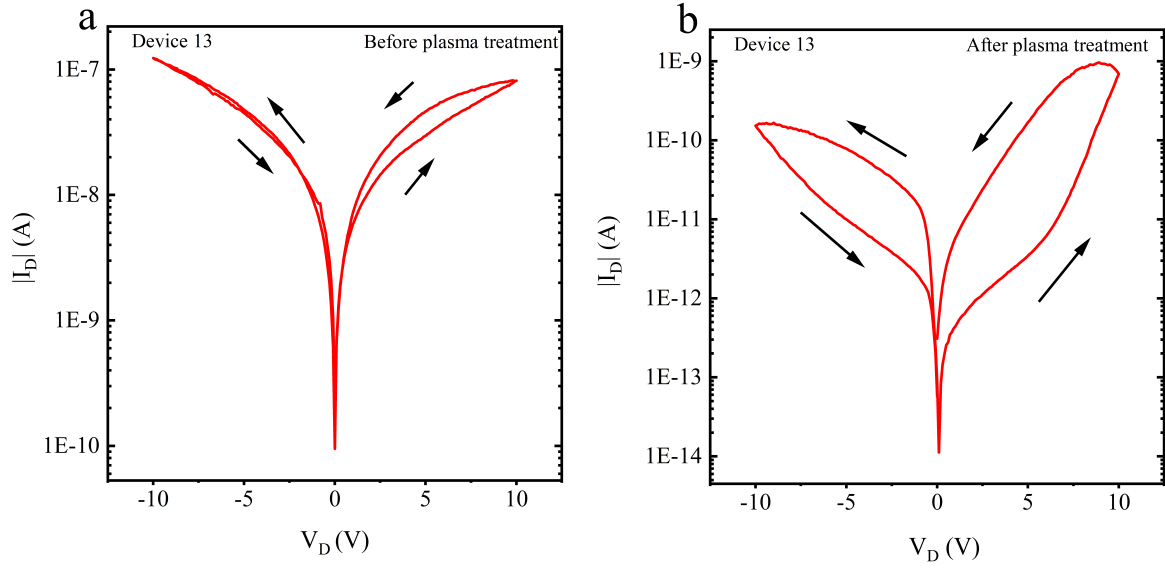


Figure S27: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

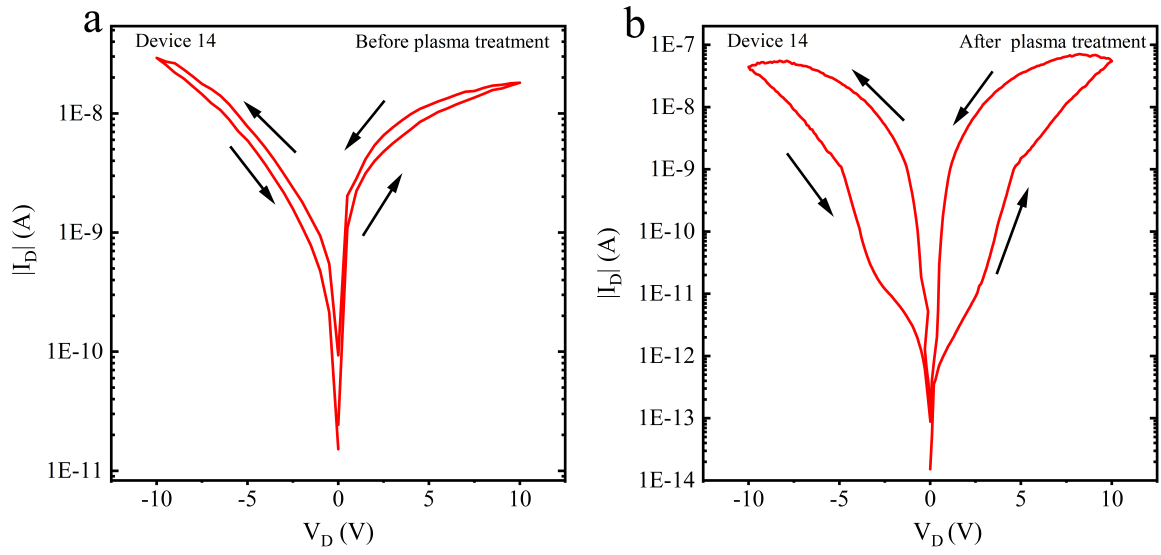


Figure S28: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

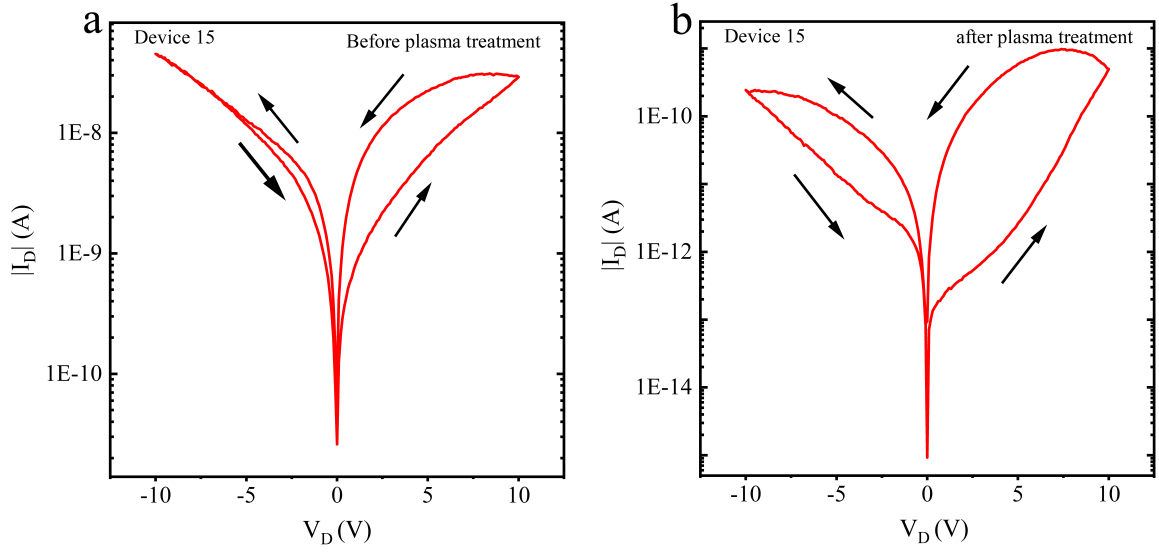


Figure S29: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

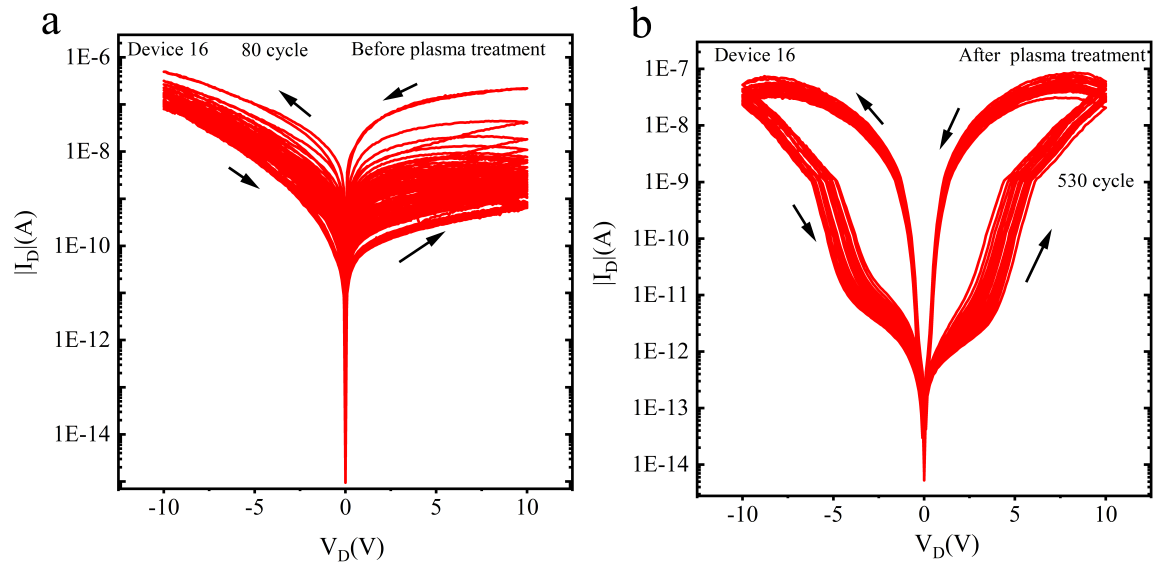


Figure S30: (a) 80 sweep cycle of I_D - V_D curve before plasma treatment (b) 530 sweep cycle of I_D - V_D after plasma treatment

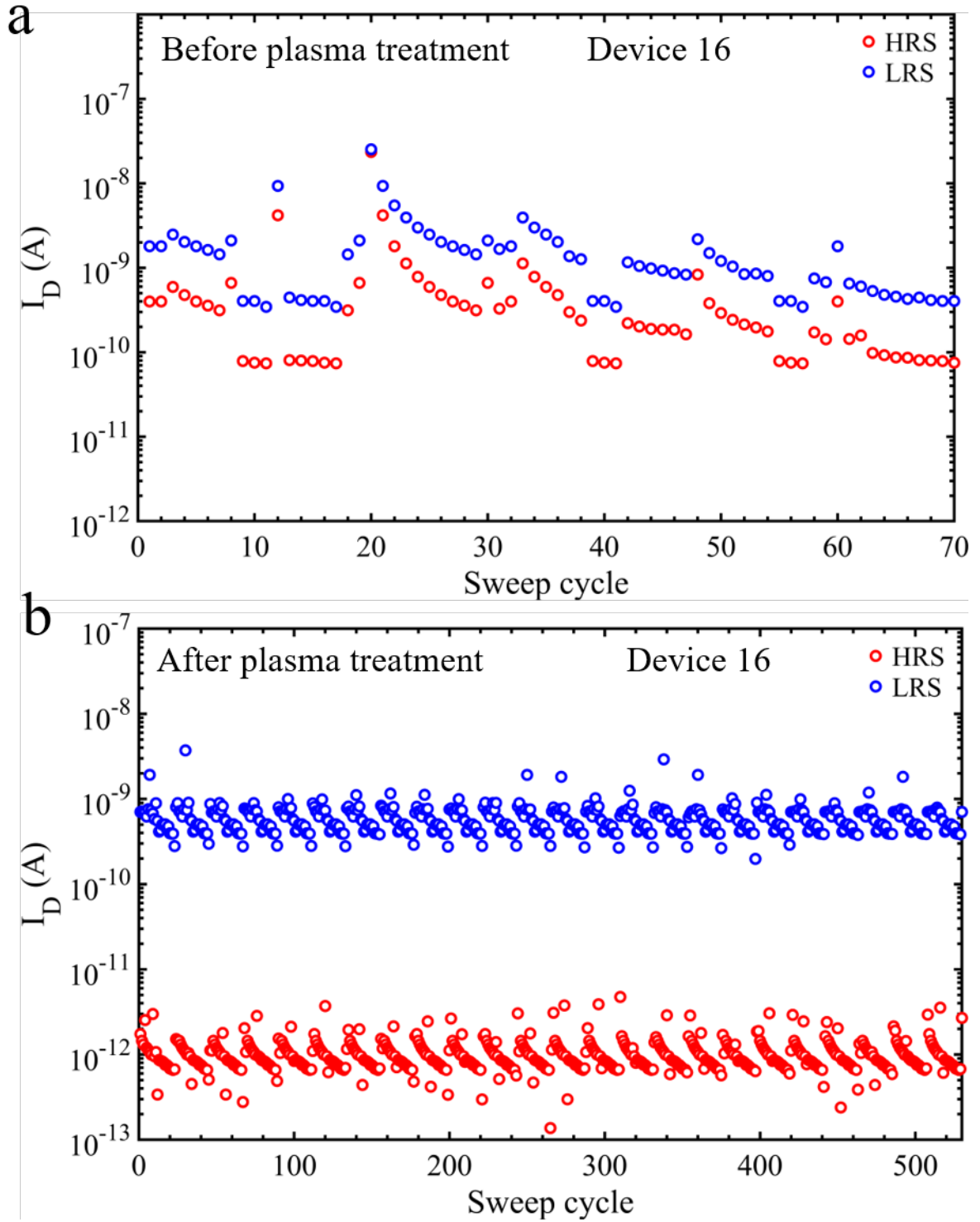


Figure S31: (a) HRS and LRS state before plasma treatment for 70 sweep cycle at $V_D = 1$ V (b) HRS and LRS state after plasma treatment for 520 sweep cycle at $V_D = 1$ V.

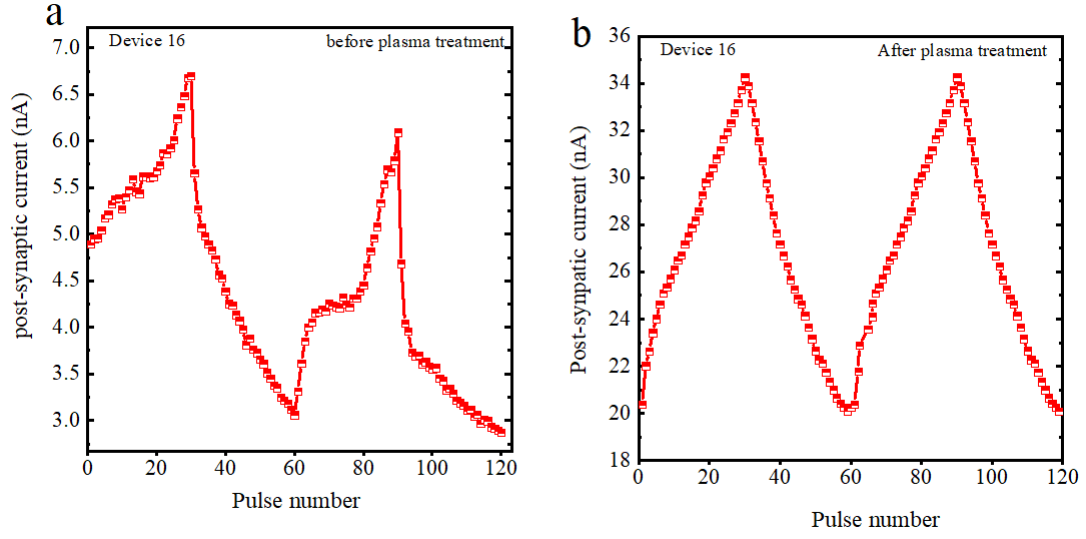


Figure S32: (a) LTP-LTD characteristics before plasma treatment (b) LTP-LTD characteristics after plasma treatment.

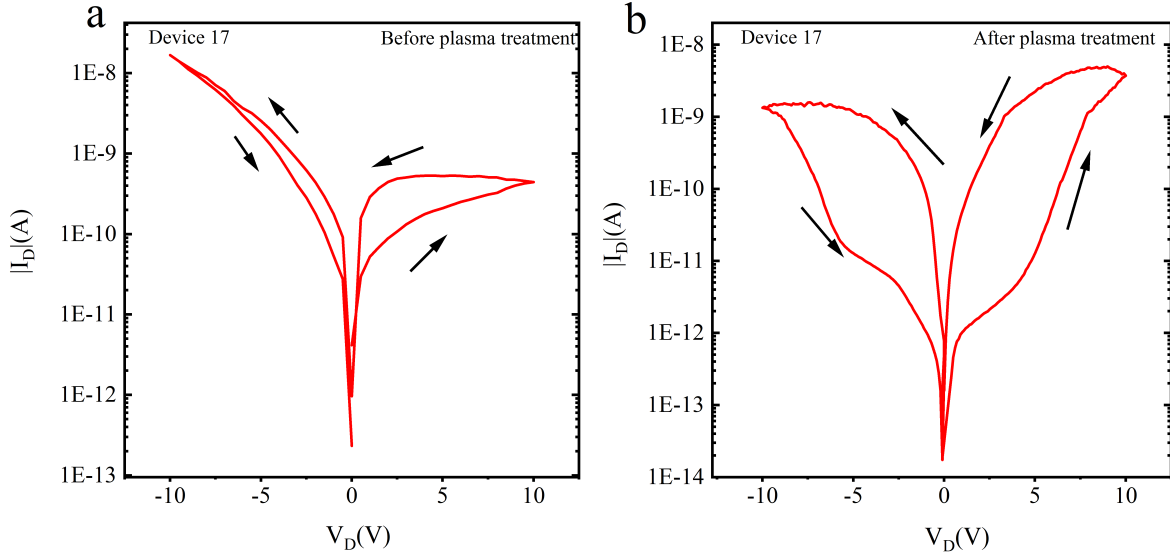


Figure S33: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

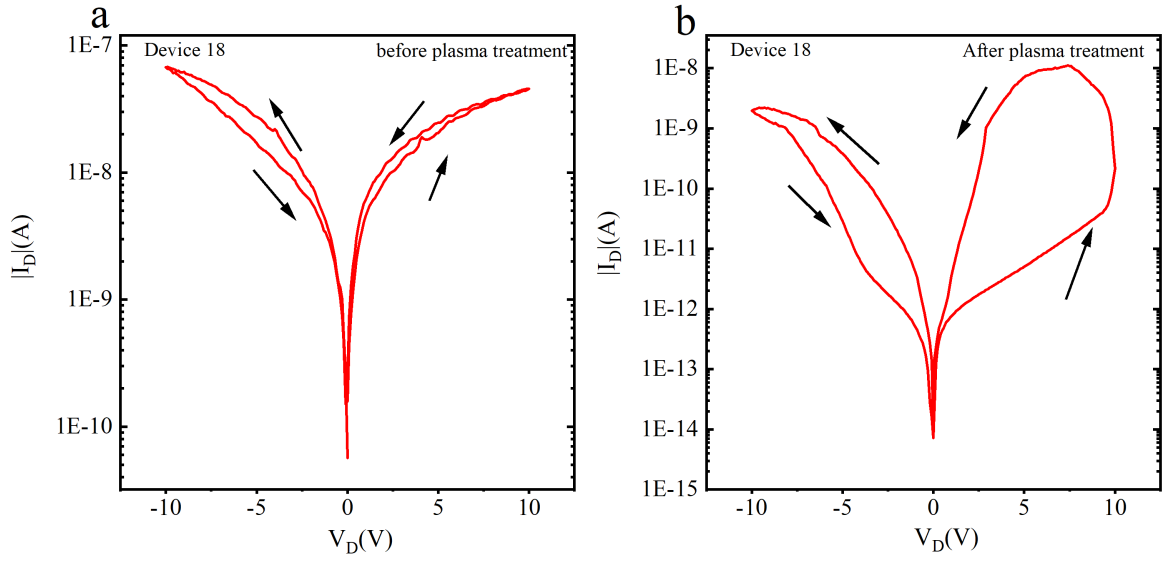


Figure S34: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

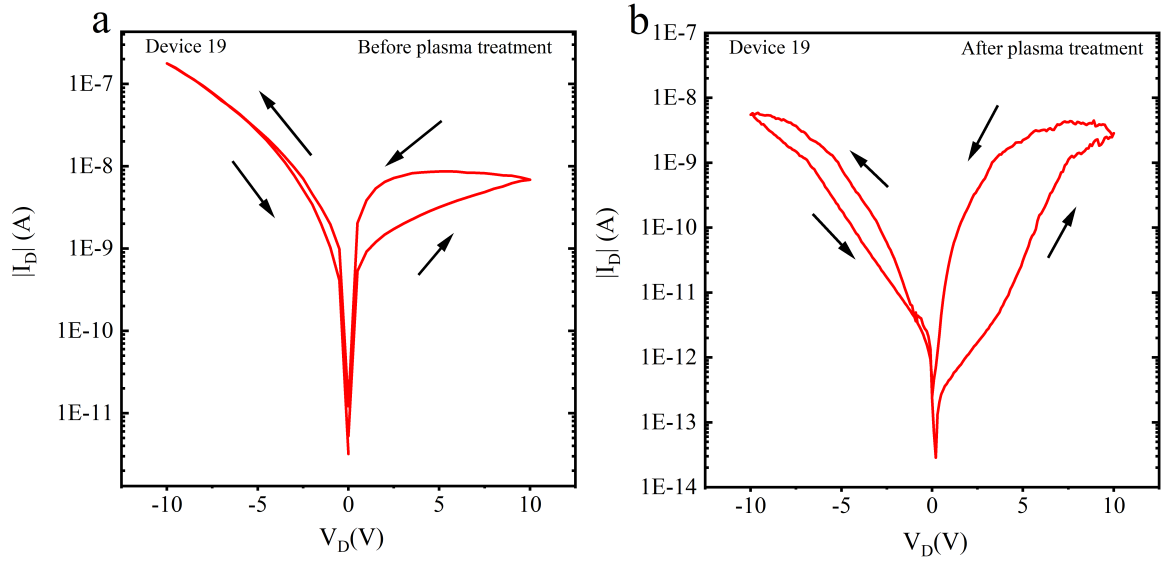


Figure S35: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

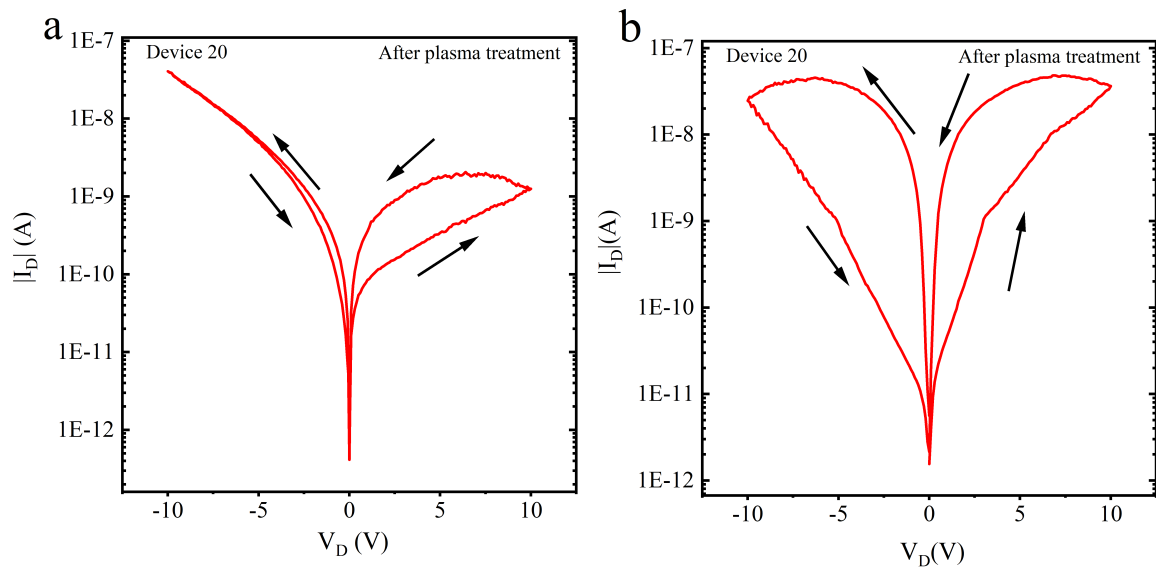


Figure S36: (a) I_D - V_D before plasma treatment (b) I_D - V_D after plasma treatment.

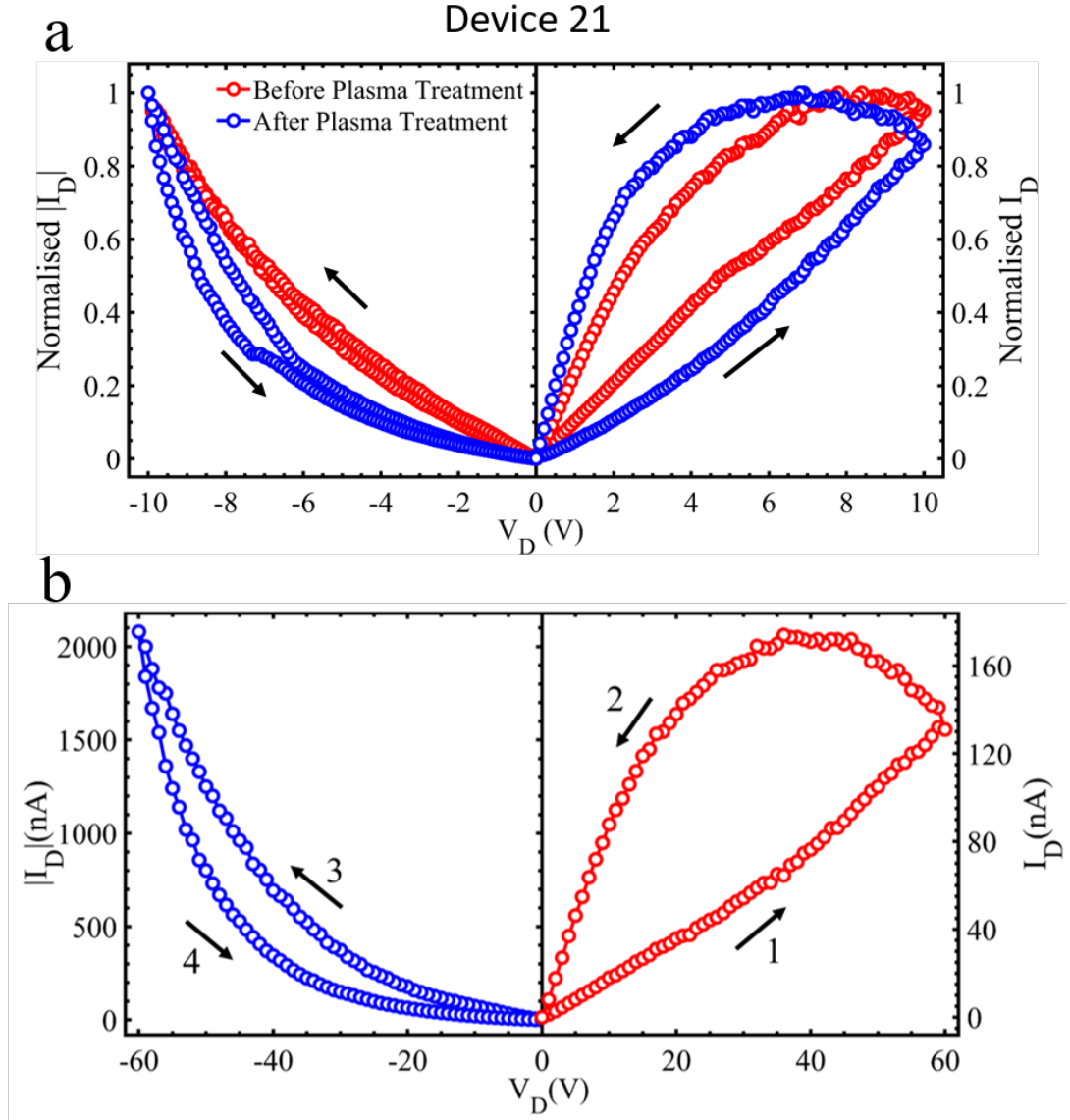


Figure S37: (a) Hysteresis comparison before and after optimal-power plasma treatment for another device (b) I_D - V_D for ± 60 V of same device after optimal-power plasma treatment at scan rate 2 V/s.

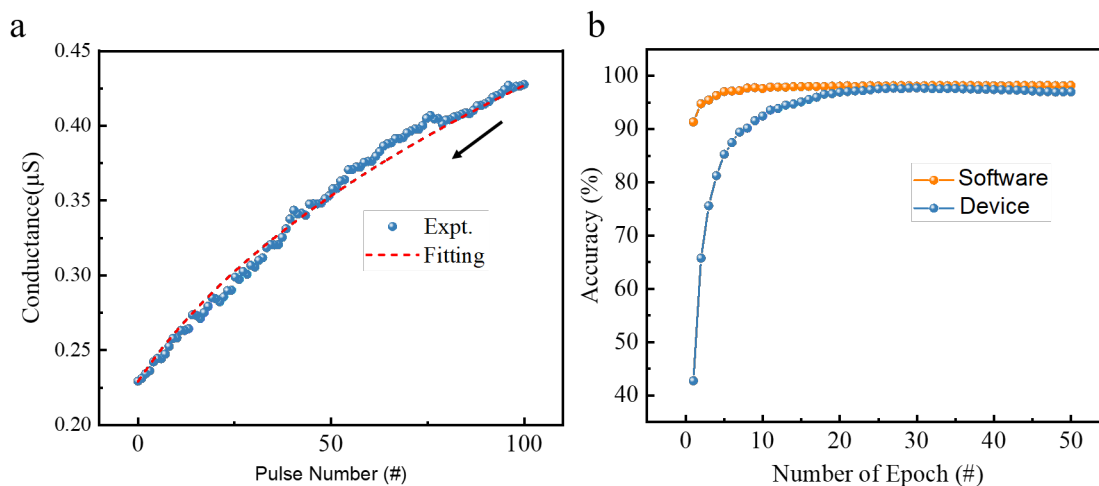


Figure S38: (a) The extracted non-linearity factors from the fitted depression curve post-plasma treatment (b) The digit recognition training accuracy of our device compared with software values.

Supplementary References

- (1) Kim, I. S.; Sangwan, V. K.; Jariwala, D.; Wood, J. D.; Park, S.; Chen, K. S.; Shi, F.; Ruiz-Zepeda, F.; Ponce, A.; Jose-Yacamán, M.; Dravid, V. P.; Marks, T. J.; Hersam, M. C.; Lauhon, L. J. Influence of stoichiometry on the optical and electrical properties of chemical vapor deposition derived MoS₂. *ACS Nano* **2014**, *8*, 10551–10558.
- (2) Stewart, T. B.; Fleischauer, P. D. Chemistry of sputtered molybdenum disulfide films. *Inorganic Chemistry* **1982**, *21*, 2426–2431.
- (3) Anwar, M.; Hogarth, C. A.; Bulpett, R. Effect of substrate temperature and film thickness on the surface structure of some thin amorphous films of MoO₃ studied by X-ray photoelectron spectroscopy (ESCA). 1989.
- (4) McCreary, K. M.; Hanbicki, A. T.; Sivaram, S. V.; Jonker, B. T. A- and B-exciton photoluminescence intensity ratio as a measure of sample quality for transition metal dichalcogenide monolayers. *APL Materials* **2018**, *6*, 111106.
- (5) Baker, M. A.; Gilmore, R.; Lenardi, C.; Gissler, W. XPS investigation of preferential

- sputtering of S from MoS_2 and determination of MoS_x stoichiometry from Mo and S peak positions. *Applied Surface Science* **1999**, *150*, 255–262.
- (6) Lince, J. R.; Carre, D. J.; Fleischauer, P. D. Effects of argon-ion bombardment on the basal plane surface of molybdenum disulfide. *Langmuir* **1986**, *2*, 805–808.
- (7) Mignuzzi, S.; Pollard, A. J.; Bonini, N.; Brennan, B.; Gilmore, I. S.; Pimenta, M. A.; Richards, D.; Roy, D. Effect of disorder on Raman scattering of single-layer MoS_2 . *Phys. Rev. B* **2015**, *91*, 195411.