

## Supplementary Information

# **High-speed energy-efficient memristor confined in sub-5 nm space with elemental oxygen reservoir layer**

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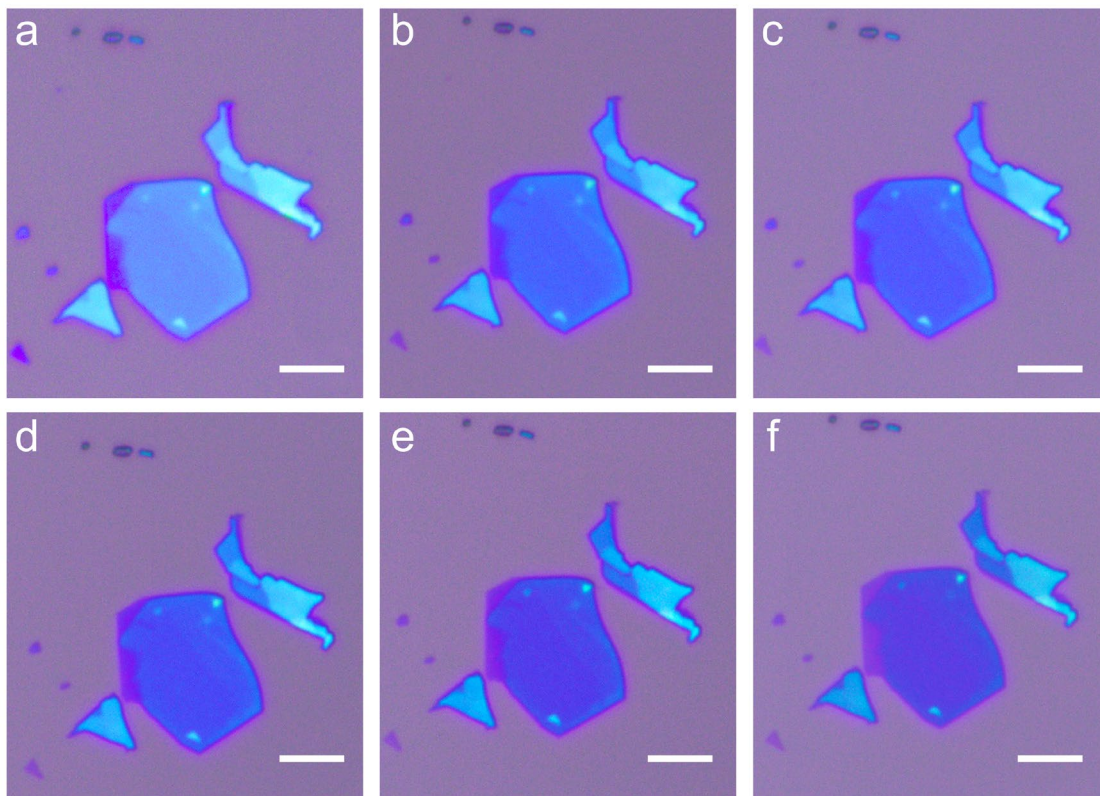
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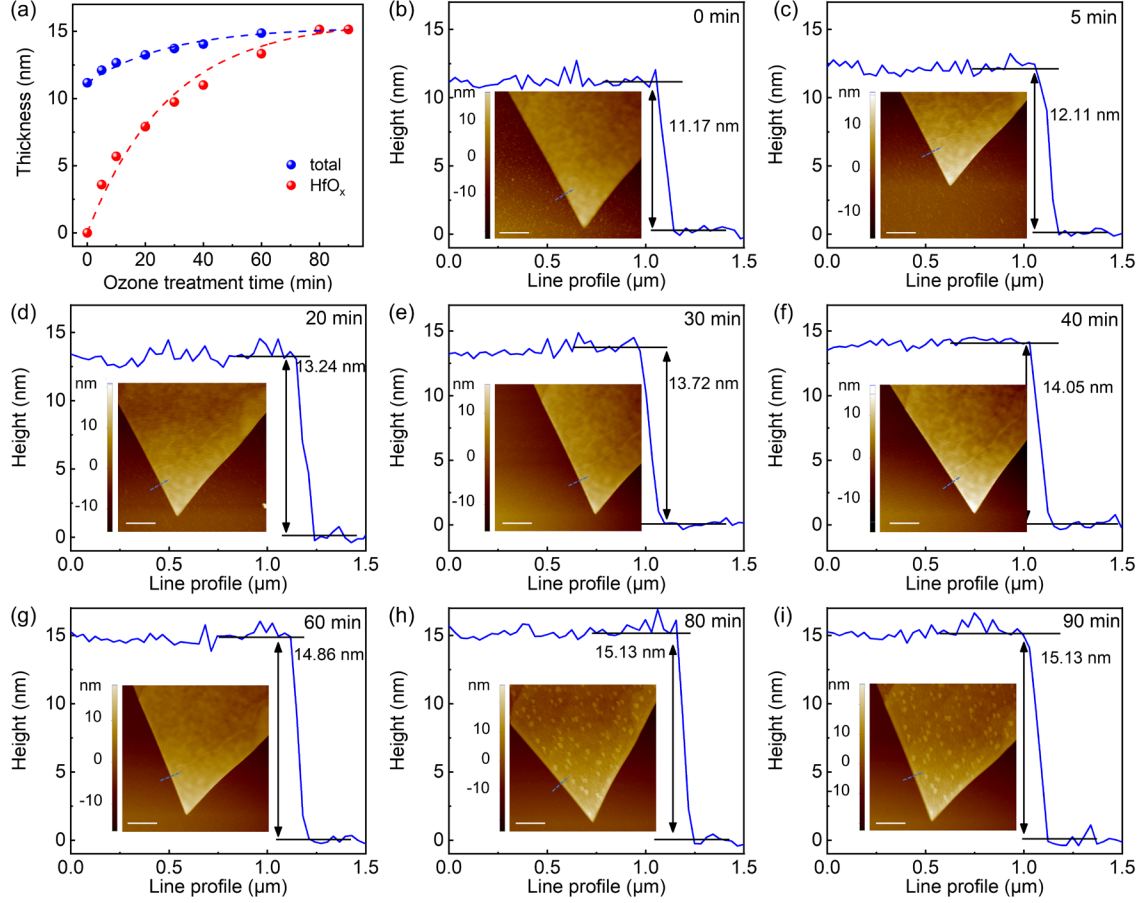
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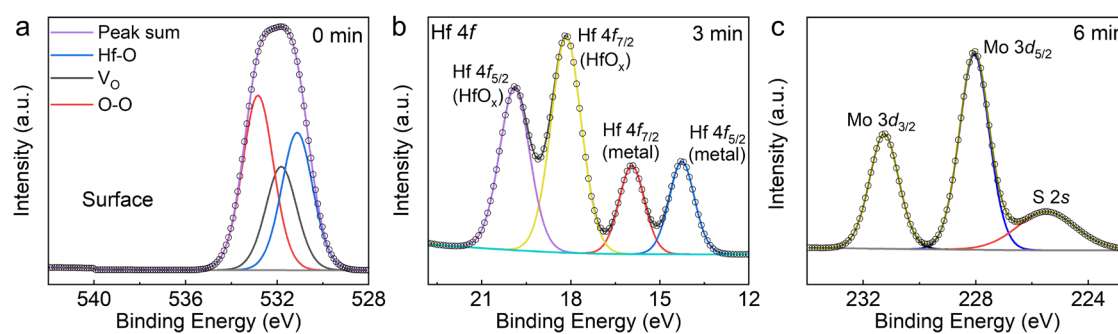
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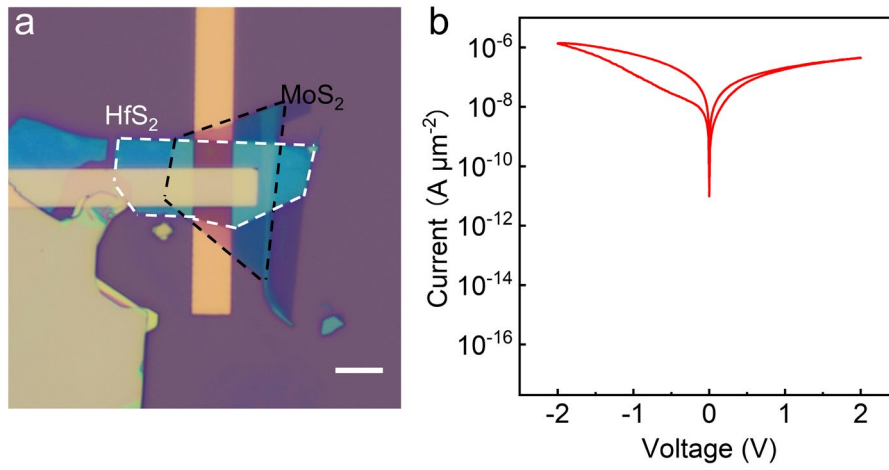
**Supplementary Fig. 1 | Optical images of HfS<sub>2</sub> flakes under different ozone treatment time. a 5 min. b 10 min. c 20 min. d 30 min. e 40 min. f 60 min. Scale bar: 5  $\mu$ m.**



**Supplementary Fig. 2 | AFM images and thickness evolution during the transformation of HfS<sub>2</sub> into HfO<sub>x</sub>.** **a** Total thickness of the HfO<sub>x</sub>/HfS<sub>2</sub>/HfO<sub>x</sub> stack and the HfO<sub>x</sub> thickness as a function of ozone treatment time. **b-i** Evolution of height profiles with varying ozone treatment time. Each inset shows an AFM image. Scale bar: 2  $\mu$ m. With increasing ozone treatment time, the HfS<sub>2</sub> flake gradually transforms from a partially oxidized state to a completely converted HfO<sub>x</sub> layer. Based on the initial thickness of HfS<sub>2</sub> (11.17 nm, Fig. 2b) and the final thickness of the fully oxidized sample (15.13 nm, Fig. 2i) measured by atomic force microscopy, the expansion ratio was determined to be 1.35. To quantify the thickness of the converted HfO<sub>x</sub> at various stages, we defined two parameters: the total AFM-measured thickness ( $t$ ) and the thickness of the residual unconverted HfS<sub>2</sub> ( $x$ ). Their relationship is expressed by the following equation:  $t = x + 1.35 \times (11.17 - x)$ . By determining the value of  $x$ , the thickness of the formed HfO<sub>x</sub> layer can be precisely derived.



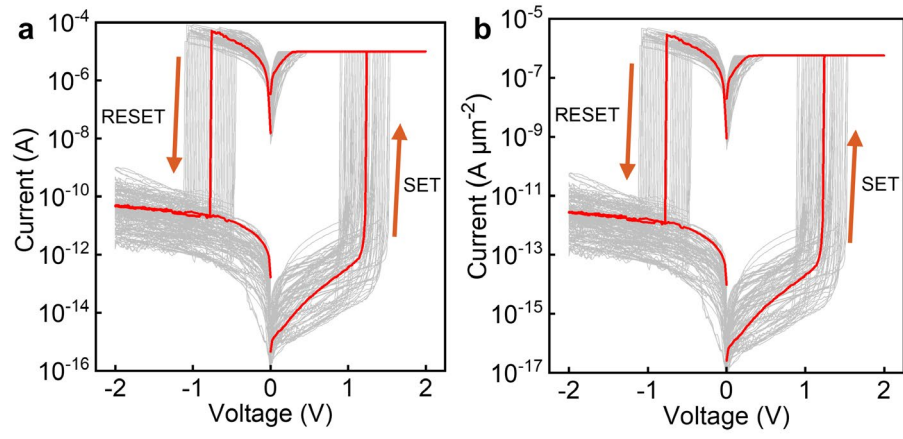
**Supplementary Fig. 3 | Depth-resolved XPS spectra. a** O 1s spectra collected at the surface. **b** Hf 4f spectrum obtained after 3 min of etching. **c** Mo 3d spectrum acquired after 6 min of etching.



**Supplementary Fig. 4 | Electrical characteristics of the control  $\text{MoS}_2/\text{HfS}_2$  device.**

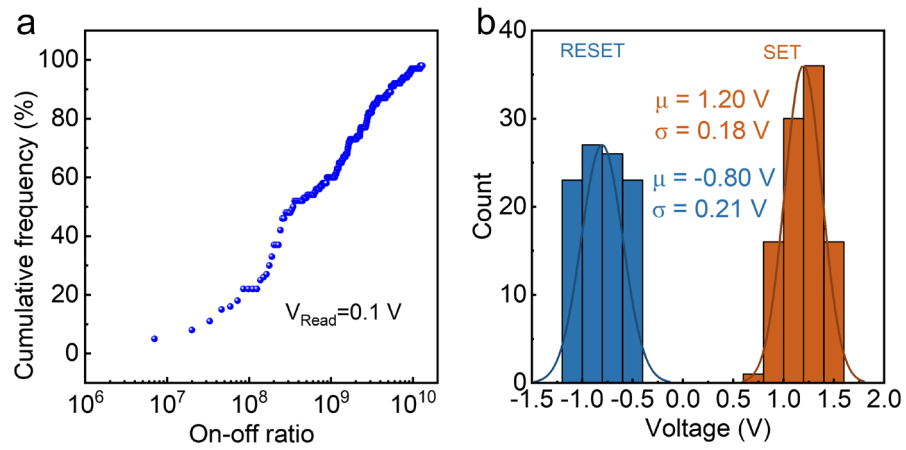
**a** Optical microscopy image of the device without ozone treatment. Scale bar: 5  $\mu\text{m}$ . **b**

I-V curves exhibiting negligible resistive switching behavior.

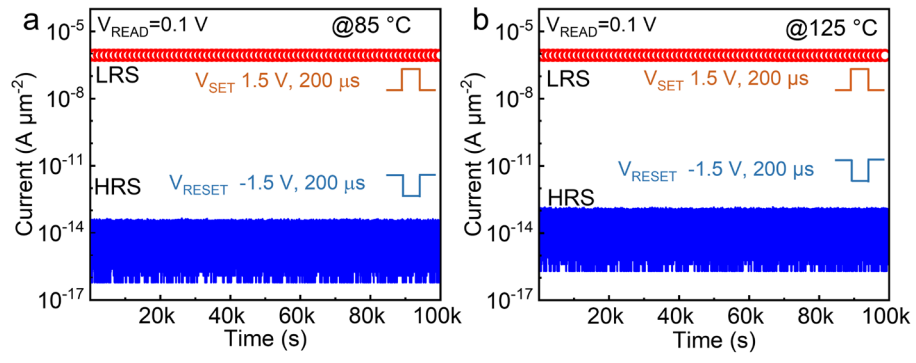


**Supplementary Fig. 5 | Electrical performance of the EOR-based memristor array.**

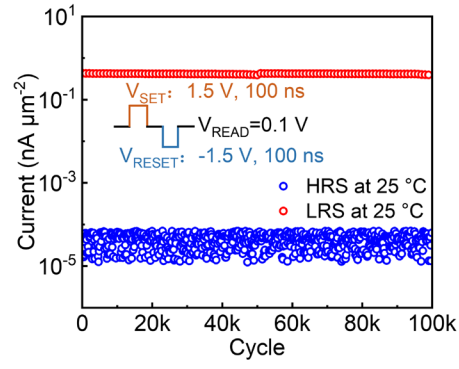
**a** Typical I-V characteristics plotted on an absolute current scale. **b** Corresponding I-V curves normalized by device area, shown as current density.



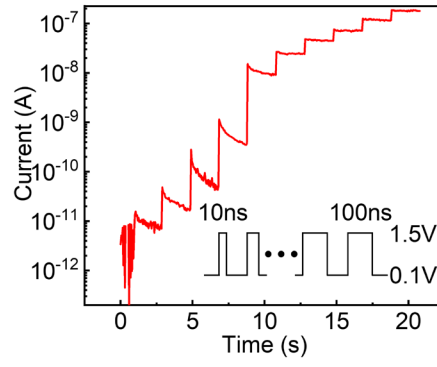
**Supplementary Fig. 6 | a** Cumulative probability distribution of the on/off current ratio extracted from I-V measurements of 100 memristors (at  $V_{\text{READ}} = 0.1 \text{ V}$ ). **b** Statistical distribution of SET and RESET voltages across 100 devices.



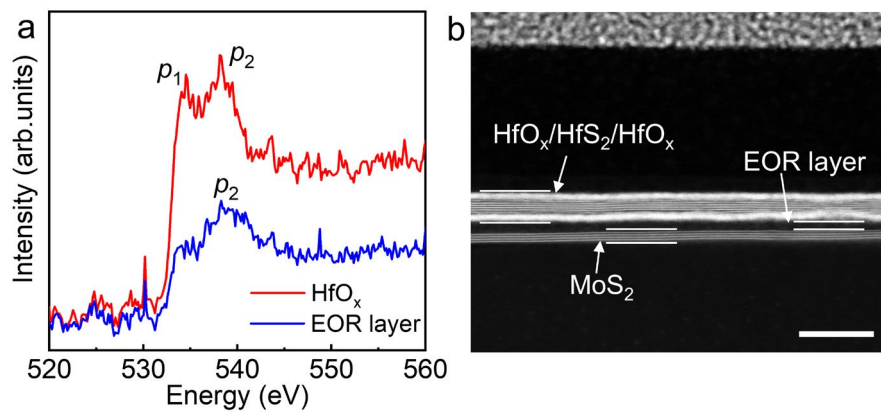
**Supplementary Fig. 7 | Retention characteristics.** Measured at (a) 85 °C and (b) 125 °C, respectively.



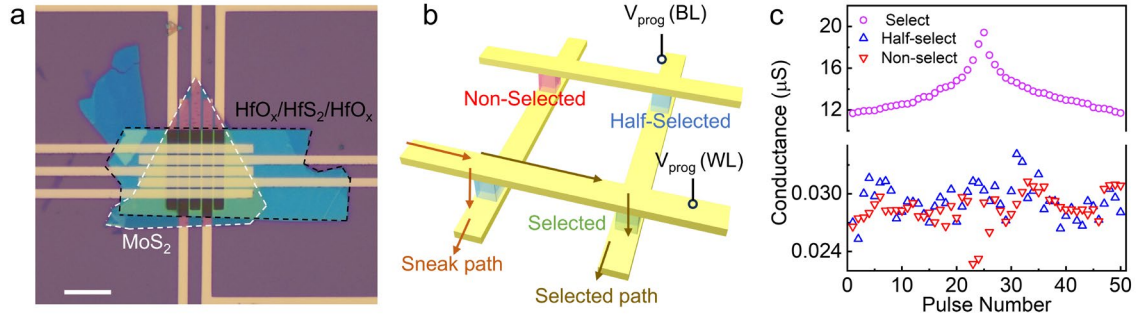
**Supplementary Fig. 8 | Endurance characteristics.** The device was monitored over  $10^5$  cycles using bipolar voltage pulses of  $\pm 1.5 \text{ V}$  (pulse width: 100 ns).



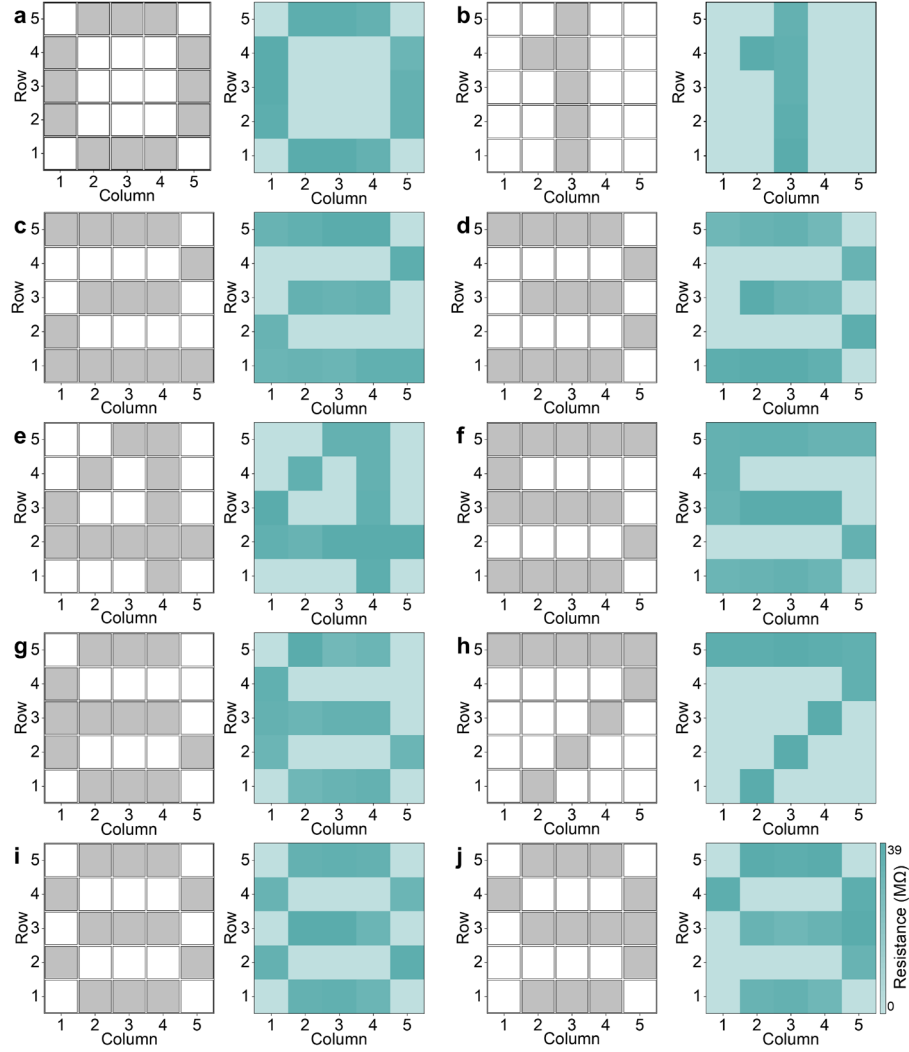
**Supplementary Fig. 9** | Read current of the EOR-based memristor measured at different pulse widths.



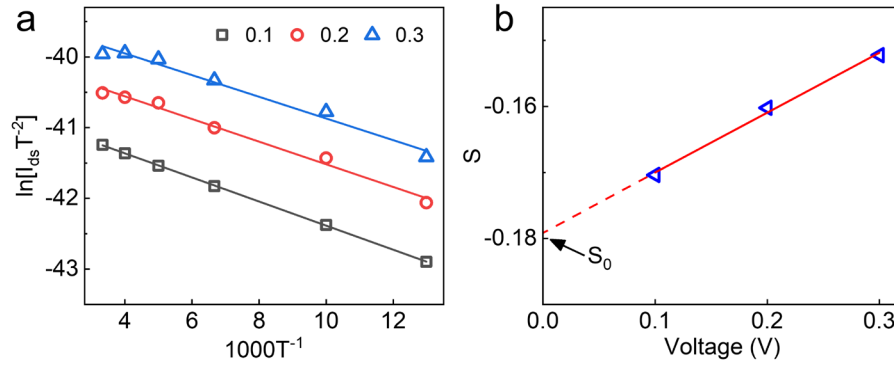
**Supplementary Fig. 10 | ELNES spectra and TEM analysis.** **a** O K-edge ELNES spectra acquired from the HfO<sub>x</sub> switching layer and the EOR layer, respectively. **b** Cross-sectional cross profile of the TEM sample. Scale bar: 20 nm.



**Supplementary Fig. 11 | Sneak-path analysis of the memristor arrays.** **a** Optical image of a  $5 \times 5$  memristor array. Scale bar:  $20 \mu\text{m}$ . **b** Schematic illustration showing the definitions of different device states within the array.  $V_{\text{prog}}$  denotes the programming voltage applied to the word lines (WLs) to induce resistive switching in the selected cell. **c** Conductance evolution of selected, half-selected, and unselected cells in the array during pulse programming ( $\pm 1.5 \text{ V}$ ,  $20 \text{ ns}$ ).



**Supplementary Fig. 12 | Demonstration of digital pattern storage in a  $5 \times 5$  crossbar memory array.** a-j Schematic diagrams (left) and corresponding experimental heatmaps (right) of the programmed patterns for digits “0” through “9”, respectively. For the schematic diagrams, the gray squares represent the high-resistance state (HRS), while the white squares represent the low-resistance state (LRS). The experimental heatmaps show the measured resistance values of each memory cell after pulse programming, where the color scale (z-axis) indicates the resistance level. The x and y axes denote the device coordinates (column and row indices). All patterns were successfully written into and read from the array, demonstrating the reliability of the device for digital data storage.



**Supplementary Fig. 13** | **a** Arrhenius plot showing the dependence of  $IT^{-2}$  on inverse temperature  $T^{-1}$ , where the solid lines represent linear fits. **b** Dependence of the extracted slope  $S$  on the bias voltage. Extrapolation to zero bias yields  $S_0$ , which is utilized to calculate the effective Schottky barrier height.

**Supplementary Table. 1** | Comparison of on/off ratio, normalized HRS current, switching time, and energy consumption with various advanced synaptic devices.

| Material                              | On/off ratio      | HRS current<br>(A $\mu\text{m}^{-2}$ ) | Switching<br>time (ns) | Energy<br>consumption (fJ) | Refs.     |
|---------------------------------------|-------------------|----------------------------------------|------------------------|----------------------------|-----------|
| HfO <sub>x</sub> /MoS <sub>2</sub>    | $1.5 \times 10^9$ | $1.5 \times 10^{-15}$                  | 8                      | 0.093 fJ                   | This work |
| MoS <sub>2</sub>                      | $10^7$            | $10^{-13}$                             | 600                    | 4.5 fJ                     | [17]      |
| 2H-MoS <sub>2</sub>                   | $10^3$            | $10^{-8}$                              | 17                     | 700 fJ                     | [24]      |
| MoS <sub>2-x</sub> O <sub>x</sub>     | $10^2$            | $10^{-4}$                              | 100                    | -                          | [10]      |
| WS <sub>2</sub>                       | $10^3$            | $10^{-10}$                             | 13                     | 299.8 fJ                   | [25]      |
| BP                                    | $3.6 \times 10^7$ | $10^{-11}$                             | 40                     | 20 pJ                      | [26]      |
| hBN                                   | $10^2$            | $10^{-10}$                             | 0.12                   | 2 pJ                       | [27]      |
| MoS <sub>2</sub> /hBN                 | $10^6$            | $10^{-12}$                             | 20                     | 3 pJ                       | [28]      |
| In <sub>2</sub> Se <sub>3</sub> /h-BN | $10^9$            | $4.2 \times 10^{-13}$                  | -                      | -                          | [29]      |
| IPS                                   | $4 \times 10^7$   | $10^{-11}$                             | 20                     | 0.056 fJ                   | [30]      |
| HfSe <sub>x</sub> O <sub>y</sub>      | $10^3$            | $6 \times 10^{-12}$                    | 50                     | 0.1 fJ                     | [31]      |
| SnS                                   | $10^8$            | $10^{-12}$                             | 1.5                    | 100 fJ                     | [32]      |
| Bi <sub>2</sub> O <sub>2</sub> Se     | $10^3$            | $10^{-9}$                              | 5                      | 3.02 pJ                    | [33]      |