Supporting Information

Configurable Multi-State Non-volatile Memory Behaviors in Ti_3C_2 Nanosheets

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Experimental section

1. Synthesis of Ti_3C_2 Nanosheets

To synthesize the Ti_3C_2 nanosheets, 2g Ti_3AlC_2 power was immersed in 30 mL 50% HF (Aladdin Reagent Co. Ltd., Shanghai, China), and stirring at 200 rpm for 24 h at room temperature (25 ^{o}C). The resulting suspensions were washed by deionized water until the pH≈5, then centrifuged at 3500 rpm to separate remaining HF. The obtained wet sediment was suspended in 30 mL DMSO striring for 18 h at room temperature, then centrifugated at 3500 rpm for 10 min to remove DMSO. Subsquently, deionized water (weight ratio of MXene to water, 1:300) were added to the residue, ultra-sonicated for 4 hours with the protection of N_2, centrifuged at 3500 rpm for 2 h. At last, the supernatant was collected for further experiments. The concentration of synthetic Ti_3C_2 solution was measured by filtering specific amounts of colloidal solution through a polypropylene filter (Tianjin Jinteng Experiment Equipment Co., Ltd, Tianjin, China), followed by overnight drying under a vacuum at 70 °C. The MXene yield-defined here as the weight of Ti_3C_2 after DMSO treatment divided by the weight of powders before HF treatment ×100-is about 21.3%.

2. Characterization of Ti_3C_2 Nanosheets and memory device

X-ray podwer diffraction (XRD) pattern spectra for Ti_3C_2 were recorded on a X Bruker D8. Raman spectra were measured by a Raman spectrometer equipped with a 473 nm laser source excitation (Lab RAM ARAMIS, Horiba Scientific). Scanning electron microscopy (SEM) was taken on field-emission scanning electron microscopy (FE-SEM, Carl Zeiss, MERLIN Compact). The transmission electron microscope (TEM) image was obtained by Tecnai F30 (FEI company) operating at 200 kV under bright-field mode. The topographic characterization was done using AFM (Bruker, Dimension Icon) under tapping mode, and the Scanasyst air tip was always kept under a clean and dry ambient atmosphere. Ultraviolet Photoelectron Spectroscopy (UPS) data was obtained using EscaLab 250Xi (ThermoFisher). The electrical properties of the Ti_3C_2-based memory device were characterized by 4200-SCS parameter analyzer (Keithley,USA) under DC sweep mode. C-AFM and KPFM were respectively carried out using SCM-PIC and SCM-PIT type tips from Bruker. The scanning rate for C-AFM in the contact mode were 0.5 Hz.

3. Preparation of the Ti_3C_2-based memory device

To fabricate Ti_3C_2 based rigid memory devices, the glass (2 cm × 2 cm) substrate coated with 185 nm thick indium tin oxide (ITO) was cleaned sequentially by Decon 90 and ultrapure water and ITO was used as BE The Ti_3C_2-PVPy mixture was obtained by dispersing a certain amount of Ti_3C_2 using 20 mg mL^{-1} PVPy DMF solution. By spin-coating at 3000 rpm for 40 seconds in the atmosphere, the Ti_3C_2-PVPy mixture was deposited onto the ITO/glass substrate and used as the active layer. After annealing at 120 ^{o}C for 120 min in a vacuum oven, the TE was fabricated by depositing 30 nm thick Al in thermal evaporator through a laser-patterned shadow mask with 4 different size electrode area (diameter: 100, 250, 500, 1000 μm). The subminiature device was fabricated using micrograte supporting film (Zhongjingkeyi (Beijing) Films Technology Co., Ltd) as shadow mask. The diameter of probe tip for subminiature device is about 0.2 μm (PL-T02, Zhanxin (Shenzhen) Technology Co., Ltd). The deposition rate of Al was 2 Å s^{-1} in the thermal evaporator. To fabricate flexible Ti_3C_2 based memory devices, a 185 nm thick ITO-coated poly(ethylene naphthalate) (PEN) substrate (175 μm thick, 2 cm × 2 cm, 6 Ω $□^{-1}$), was first cleaned by O_2 plasma for 5 min and then used as substrate. All the other aspects of the procedure remained identical. The electrical properties of the Ti_3C_2-based memory devices were characterized by Keithley 4200-SCS semiconductor parameter analyzers equipped with a PRCBE probe station with a temperature controller. Moreover, except for the cell area dependence characters, the other electrical properties, including *I-V* curves, retention and cycle, were measured using the device with a diameter about 250 μm. All the set-up was fixed on antivibration mounting. During characterization, the upper Al electrodes were applied with voltage bias, and the ITO electrodes were grounded. More than 100 devices were characterized in the electrical investigation.

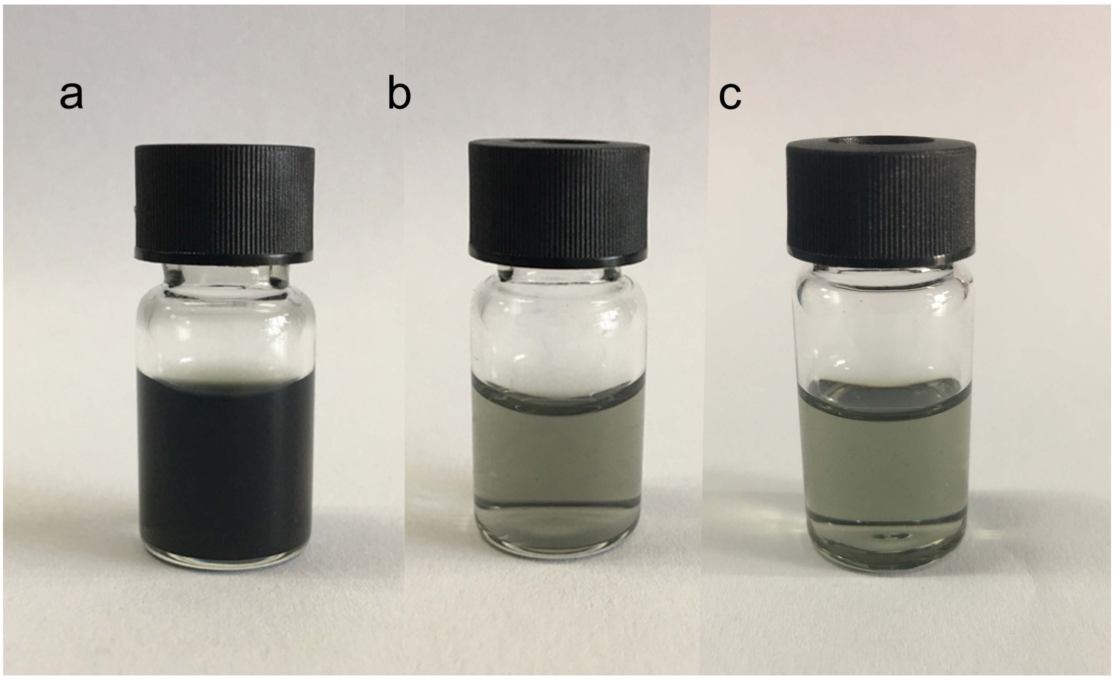

Figure S1. (a) Photograph of the MXene (Ti_3C_2) colloid solution (A, 2.5 mg mL^{-1}). (b) The mixture of Ti_3C_2 (0.24 mg mL^{-1}) and PVPy (20 mg mL^{-1}). (c) The mixture of Ti_3C_2 (0.24 mg mL^{-1}) and PVPy (20 mg mL^{-1}) after 30 days, indicating the excellent uniformity.

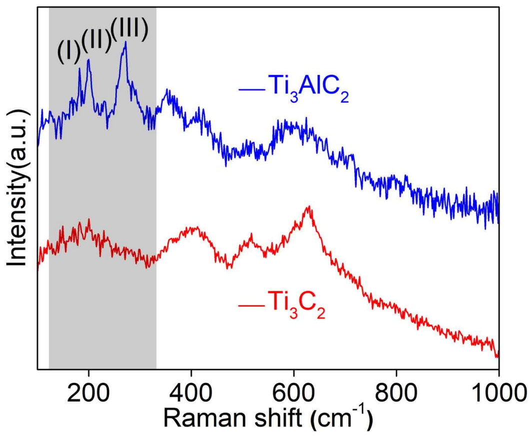

Figure S2. Raman spectra of the Ti_3AlC_2 MAX (powder) and Ti_3C_2 MXene film.

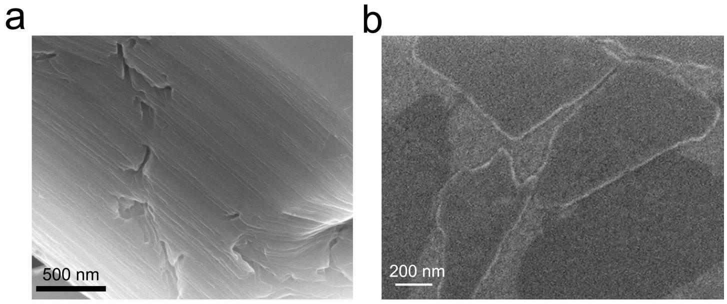

Figure S3. The SEM images of the MAX (Ti_3AlC_2) after HF treatment (a) and dispersive MXene (b).

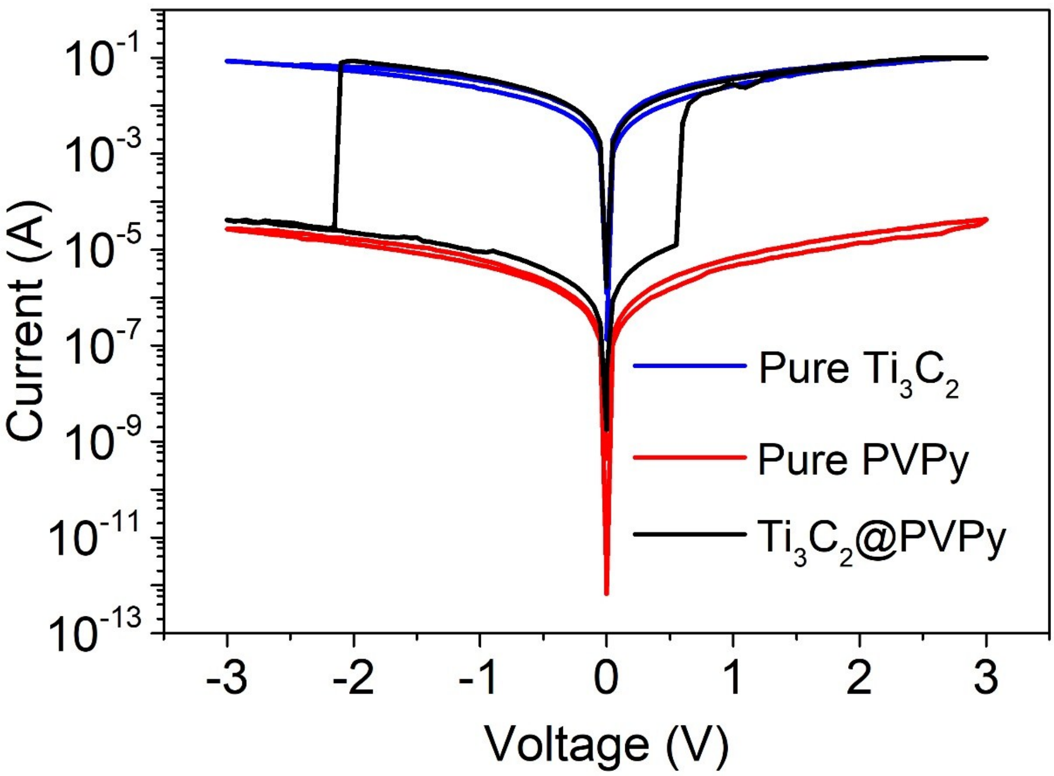

Figure S4. The *I-V* curves of pure Ti_3C_2, pure PVPy and Ti_3C_2@PVPy mixtures (PVPy: 20 mg mL^{-1}, Ti_3C_2: 0.24 mg mL^{-1}) based RRAM devices.

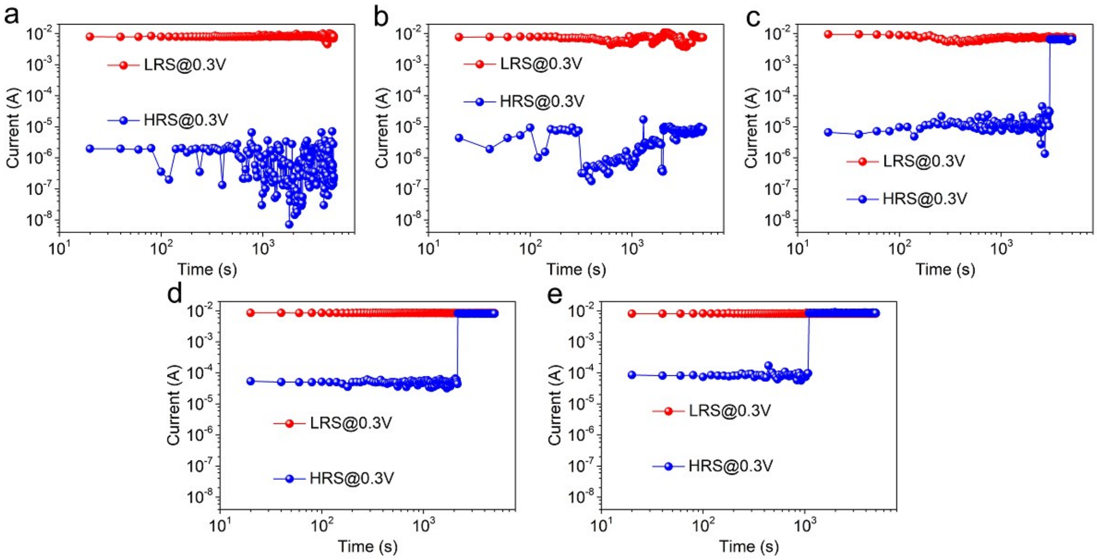

Figure S5. The retention characteres of Ti_3C_2 based RRAM under different temperatures (a: 30℃, b: 50℃, c: 70℃, d: 90℃, e: 110℃).

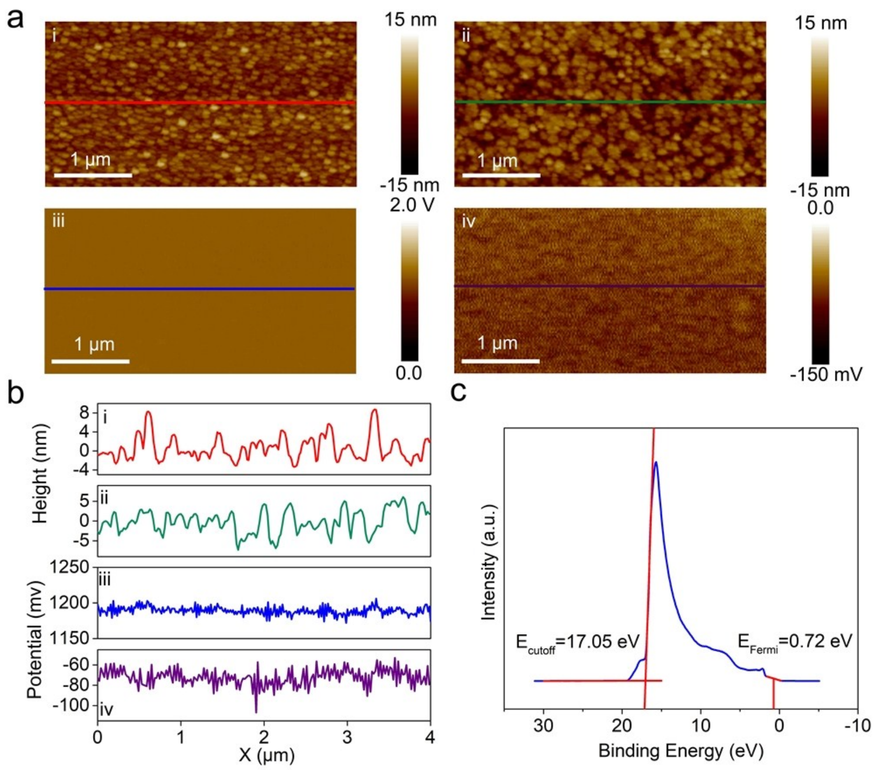

Figure S6. (a) and (b) The AFM morphology and KPFM surface potential distribution of Al (left) and ITO electrode (right). The work function of KPFM tip is about 5.0 eV. Therefore, the work function of Al and ITO could be calculated to be 3.9 eV and 5.1eV according to $V_{CPD}=V_{Sample}-V_{Tip}$. c) The UPS image of MXene (Ti_3C_2) nanosheet. (According to the Figure 3c (E_{cutoff}=17.08 eV, E_{Fermi}=0.77 eV) and the formula φ_{MXene} = hn-(E_{Cutoff} -E_F), φ_{MXene} = 21.2 eV- (17.08 eV- 0.77 eV) =4.91 eV).

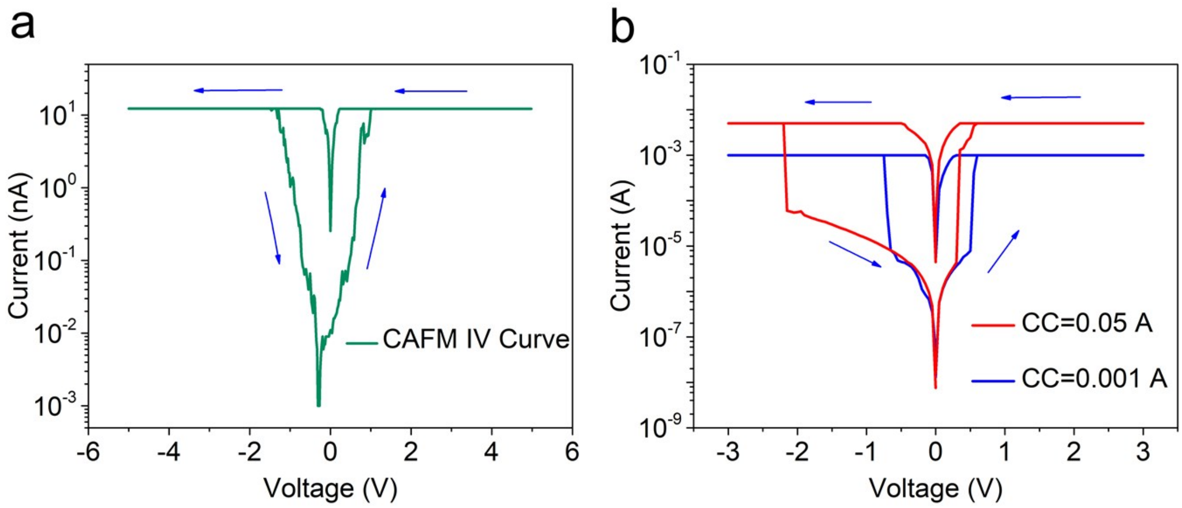

Figure S7. The *I-V* curves collected by C-AFM using Ramp program (a) and probe station (b).

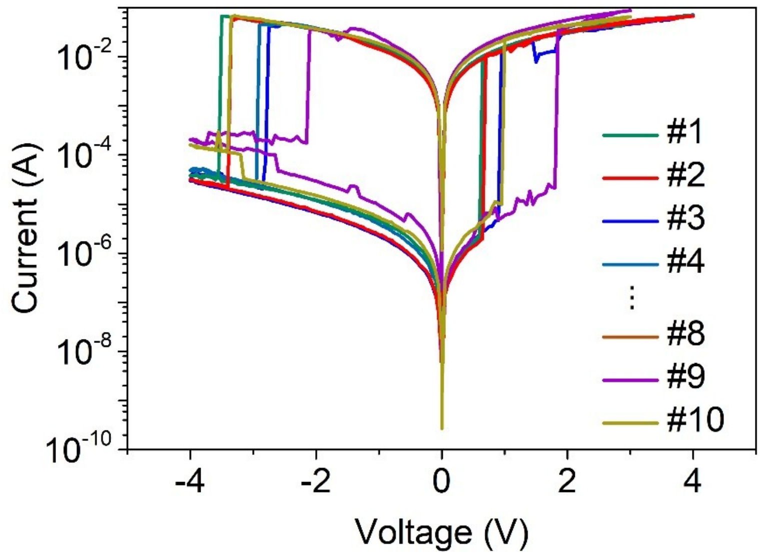

Figure S8. The *I-V* curves of the small size cross-point Ti_3C_2 based devices (100 μm).

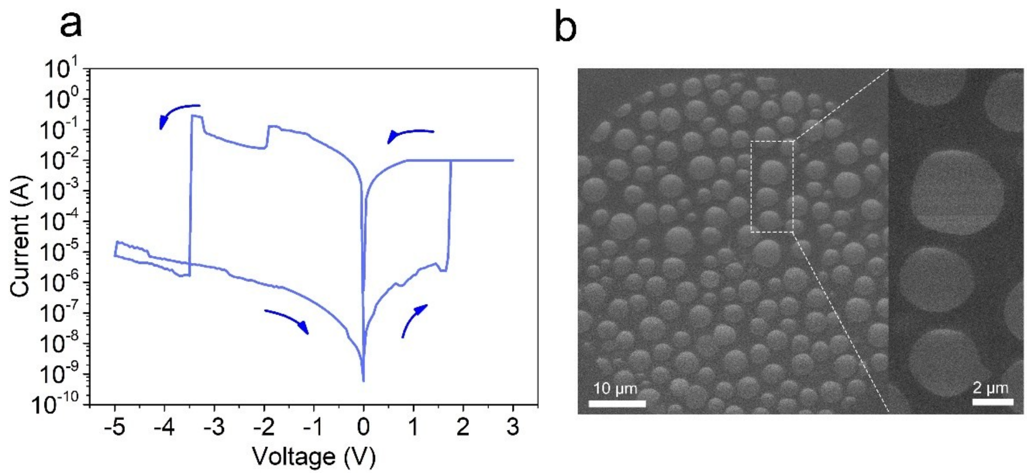

Figure S9. a) The *I-V* curve of small size device (diameter: 3-5μm) collected using probe station. b) The pictures of small size device collected by SEM; The subminiature device was fabricated using micrograte supporting film (Zhongjingkeyi(Beijing) Films Technology Co., Ltd) as shadow mask; The diameter of probe tip for subminiature device is about 0.2 μm (PL-T02, Zhanxin (Shenzhen) Technology Co., Ltd).

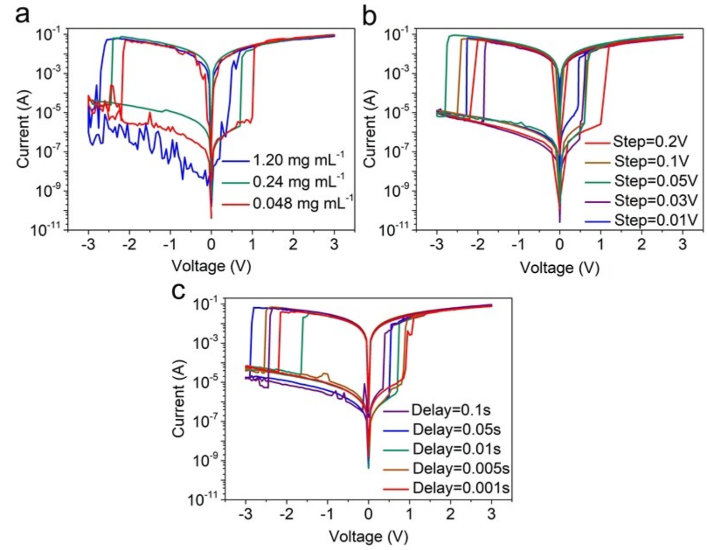

Figure S10. a) The *I*-*V* curves of memories with different Ti_3C_2 concentrations. b) The *I*-*V* curves of RRAM with different voltage step. c) The *I*-*V* curves of memories with different delay times.

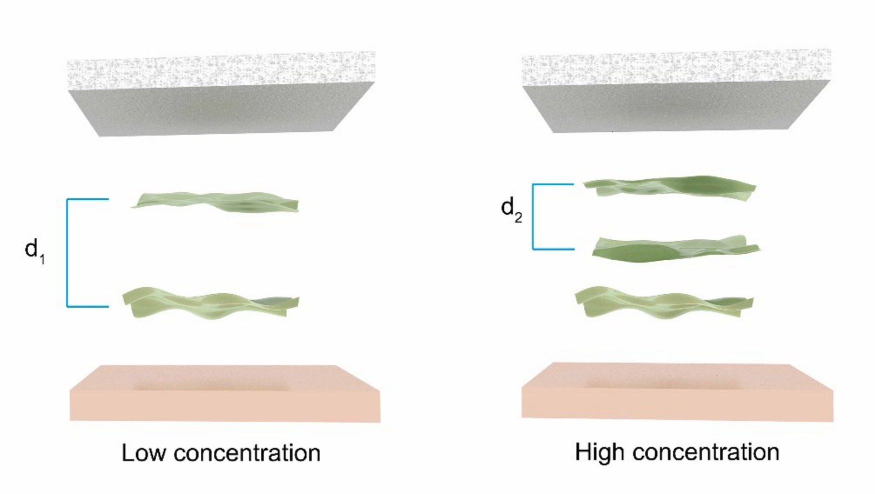

Figure S11 The schematic diagram of the distance of traps on adjacent nanosheets (d_2<d_1).

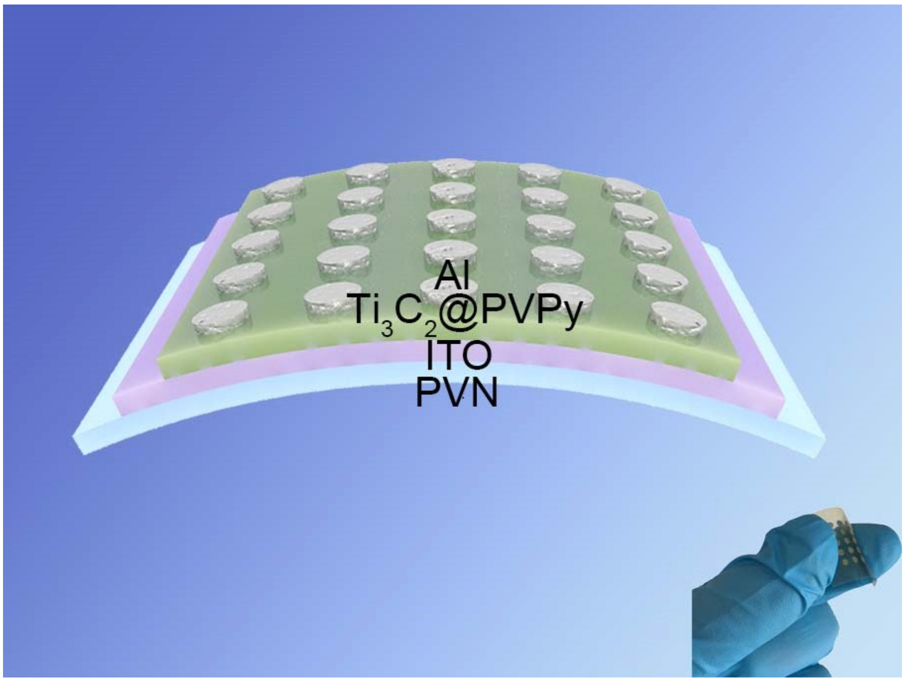

Figure S12. Schematic of the PEN/ITO/Ti_3C_2@PVPy/Al (inset: the optical image of Ti_3C_2 memory devices fabricated on flexible substrate).

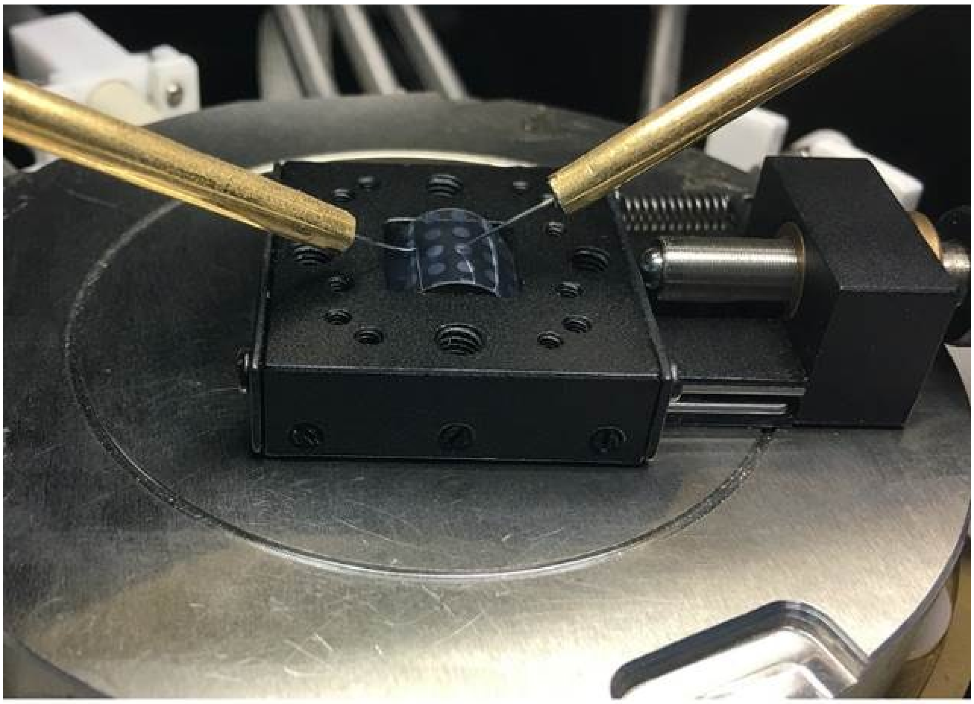

Figure S13. Illustration of test condition during the bending test (the measured devices were near the middle of the sample).

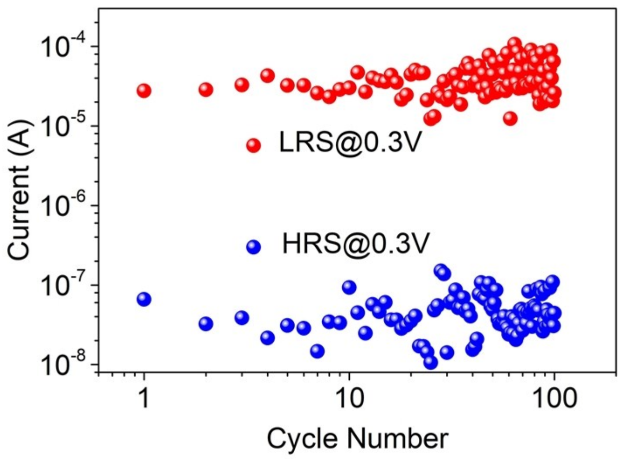

Figure S14. The reliability of the Ti_3C_2-based flexible memories.

Table S1. The summary of the electrical performances of RRAMs based on 2D materials in recent years

Device structure	Memory effect	V_{SET} (V)	ON/OFF ratio	Journal name
Ag/MoS_2@PVA/Ag	Rewritable	3	1.28×10^2	Sci. Rep.[1]
Al/2H-MoS_2@PVP/ITO	Rewritable	0.7	10	Small[2]
Al/1T@2H-MoS_2@PVP/ITO	WORM	1.24	2×10^2	Small[2]
Ag/WS_2/Ag	Rewritable	2	10^3	Semicond. Sci. Tech.[3]
Ggraphene/hBN/Ggraphene	Rewritable	2.7	10^3	2D Mater.[4]
Ag/hBN/Au	Rewritable	-1.3	1×10^2	2D Mater.[5]
Au/$BaTiO_3$/$MoSe_2$/SiO_2/Si/Al	Rewritable	0.6	1×10^2	J. Mater. Chem. C[6]
Ag/hBN/Cu foil	Rewritable	0.72	1×10^2	Adv. Funct. Mater.[7]
ITO/hBN/graphene	Rewritable	0.66	4.8×10^2	ACS Nano[8]
Al/MoS_2@PCBM/ITO	WORM	2	3×10^2	ACS Appl. Mater. Inter.[9]
Al/Ti_3C_2@PVPy/ITO	Rewritable	0.5	10^4	This work

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