Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

to

Evaluating charge-type of polyelectrolyte as dielectric layer in memristor and synapse emulation

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Detail Experiments

Preparation of polyelectrolyte-based devices: The memristor device, which was also for simulating synaptic function, was prepared on the conductive glass substrate of indium tin oxide (ITO) purchased from Guro Glass Company, and the aqueous solution of polyacrylic acid 50% (PAA, Mw=3000) and polyethyleneimine 50% (PEI, Mw=750,000) used for its dielectric layer were purchased from Aladdin Reagent (Shanghai) Co. Firstly, the ITO was cut into the size of 1.5×2 cm^2, then the substrates were ultrasonicated with deionized water, acetone, and ethanol for 30 min each time, respectively. Then they were dried with nitrogen and left at room temperature for 24 h to ensure sufficient drying. Before using as substrate, they were also treated in an ozone environment for 30 min. 50wt% aqueous solution of PAA and PEI were diluted using deionized water to 0.25wt% and 0.5wt%, and added Calcium Chloride ($CaCl_2$) to prepare precursor solution with a molar ratio of functional group (-COOH or $-NH_2$) : Ca^{2+} as 1:1. The mixing solution was ultrasonicated and stirring for 6h to make a clear solution. The polyelectrolyte films were prepared by spin coat the solution onto the ITO conductive glass substrate at 3000 rpm for 30s. The thickness of polyelectrolyte film was further adjusted by repeating above process after leaving the as prepared polyelectrolyte film at 60 °C for 15 min to dry. Finally, the ITO top electrode was deposited by magnetron sputtering using a 150μm aperture mask version, and the growth conditions were 95 mm distance between the ITO target and the substrate with 4 sccm : 40 sccm oxygen/argon ratio, 0.4 Pa working pressure, and 40 min growth time.

Characterizations: Electrical characteristics were carried out by using a semiconductor parameter analyzer (Anjie B1500) with an Agilent pulse generator. During the test, a

voltage is applied to the top electrode ITO and the bottom electrode ITO is grounded. For the I-V characteristics tests, an electroforming process is initially required to activate the ITO/PAA-Ca^{2+}/ITO sample, after which the I-V scan is performed at -1.5V and 3V and the I-V curves flatten out. Endurance tests are carried out using a continuous DC scan. Retention tests are performed at room temperature and 85°C, respectively. The reading voltage of both endurance and retention tests is the same as 0.1 V. A series of synaptic functions of the device are measured using the pulse module, where different synaptic functions are achieved by applying different conditions and different number of pulse voltages.

An atomic force microscopy (AFM) topographic images and peak force tunneling atomic force microscopy (PFTUNA) analysis were carried out using Dimension Icon (Bruker AXS). The transmission spectra in the visible range (300-800 nm) were measured using a PerkinElmer Lamb-da 750 UV/VIS/NIR spectrometer. The cross-section images and EDS mapping images of the thin films were observed by the energy dispersive analysis of X-rays (EDX, JEOL) attached with field emission scanning electron microscopy (FESEM, ZEISS MERLIN Compact). X-ray photoelectron spectroscopy (XPS) was performed using ESCALAB 250XI (Thermo Scientific).

Additional Figures

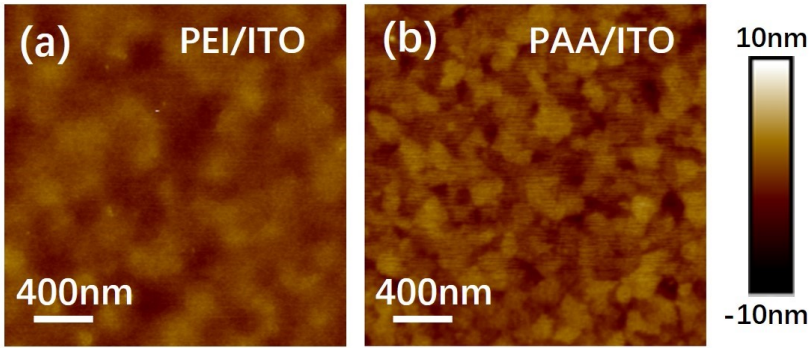

Figure S1. AFM topographic images of (a) PEI/ITO, and (b) PAA/ITO surfaces.

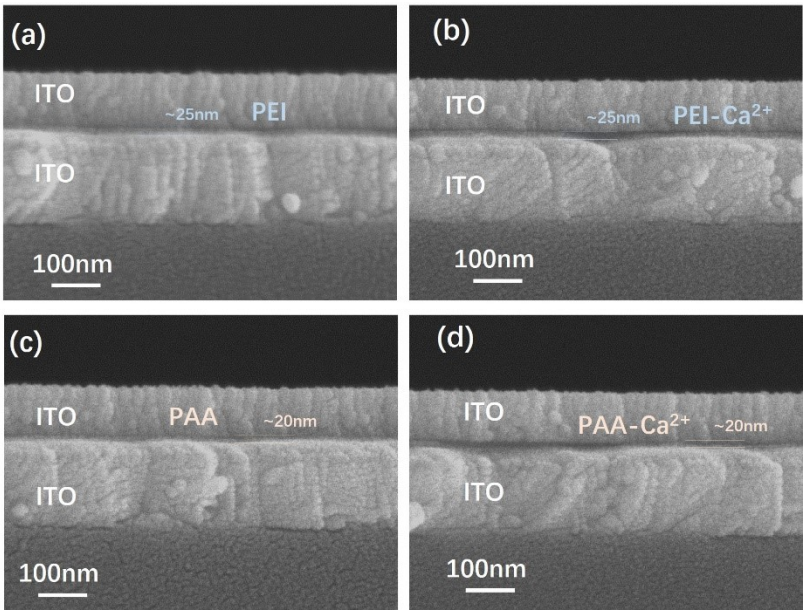

Figure S2. SEM cross-section images of (a) ITO/PEI/ITO, (b) ITO/PEI-Ca^{2+}/ITO, (C) ITO/PAA/ITO and (d) ITO/PAA-Ca^{2+}/ITO.

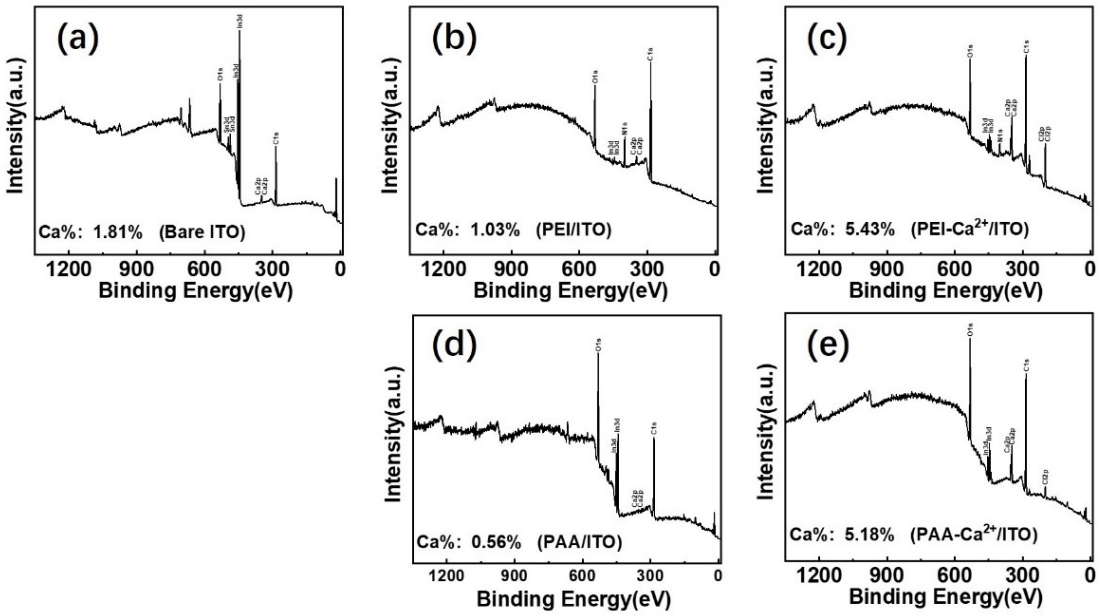

Figure S3. XPS spectrum of the (a) Bare ITO, (b) PEI/ITO, (c) PEI-Ca^{2+}/ITO, (d) PAA/ITO and (e) PAA-Ca^{2+}/ITO (insert is atomic percent of Calcium).

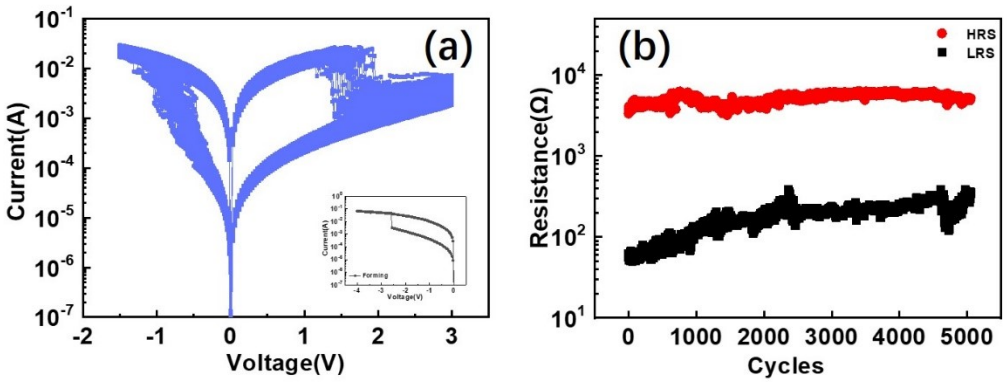

Figure S4. (a) the 100 I–V sweeps from a PAA-Ca^{2+} memory device and (b) its endurance performance.

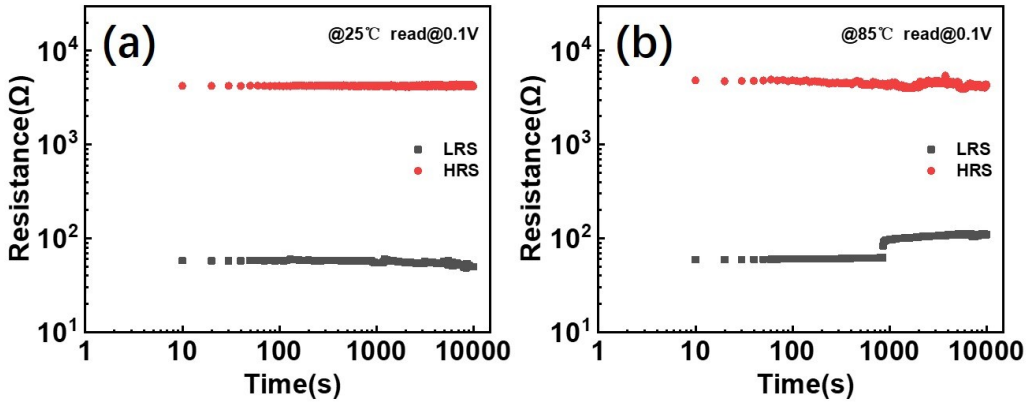

Figure S5. Retention characteristics of PAA-Ca^{2+} memory device at (a) room temperature and (b) 85℃.

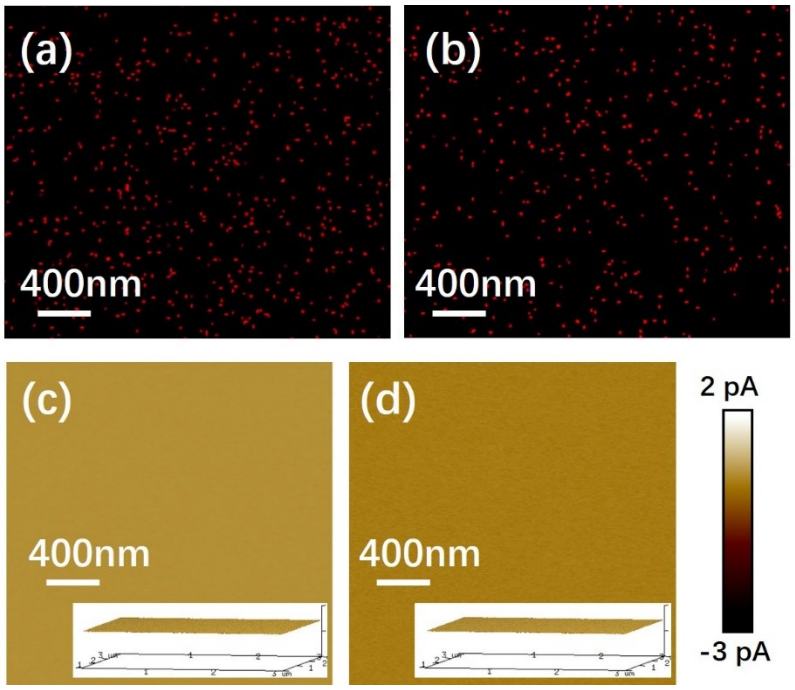

Figure S6. EDS mapping images of PEI-Ca^{2+} device: (a) before setting, (b) after setting; and PFTUNA current mapping images of PEI-Ca^{2+} device (insert is the 3D image): (c) before setting, (d) after setting.

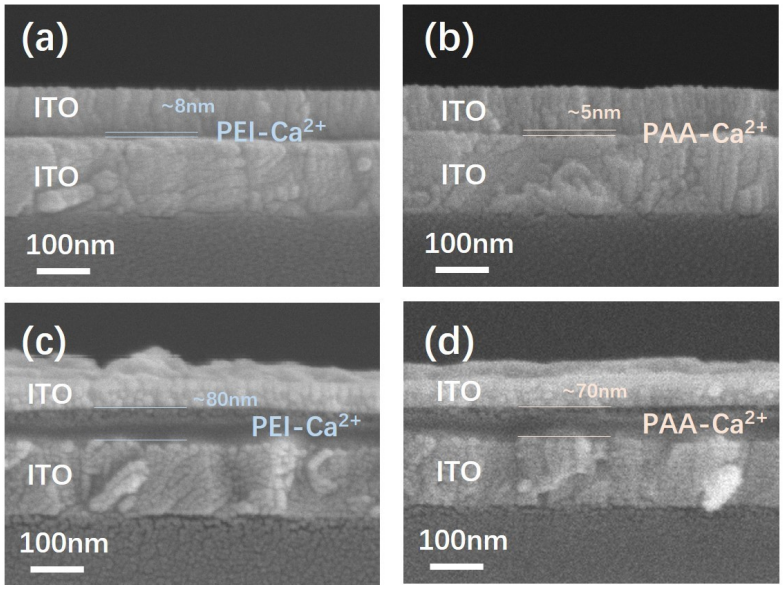

Figure S7. SEM cross-section images of (a) ITO/PEI-Ca^{2+} (8nm)/ITO, (b) ITO/PAA-Ca^{2+} (5nm)/ITO, (C) ITO/PEI-Ca^{2+} (80nm)/ITO and (d) ITO/PAA-Ca^{2+} (70nm)/ITO.

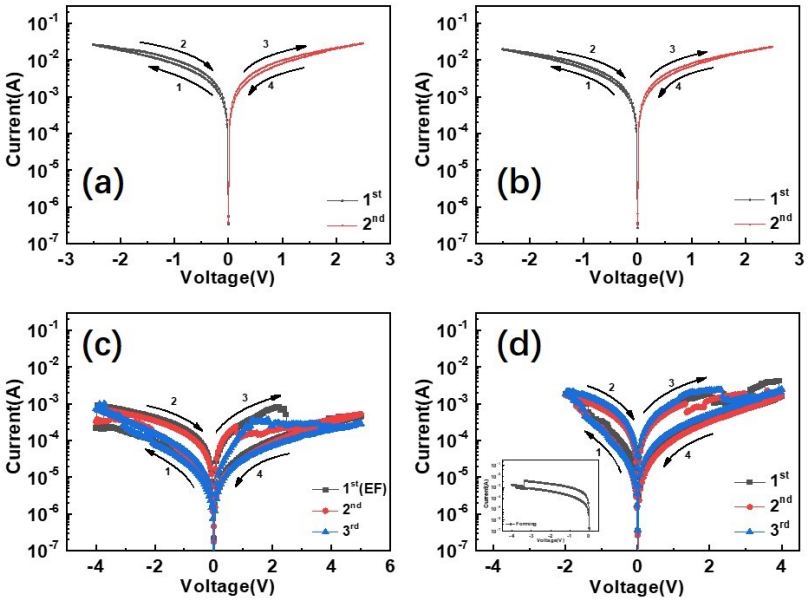

Figure S8. Current–voltage characteristics of (a) ITO/PEI-Ca^{2+} (10nm)/ITO, (b) ITO/PAA-Ca^{2+} (10nm)/ITO, (C) ITO/PEI-Ca^{2+} (80nm)/ITO and (d) ITO/PAA-Ca^{2+} (70nm)/ITO, the inset figure displays an electroforming curve in a negative bias region.

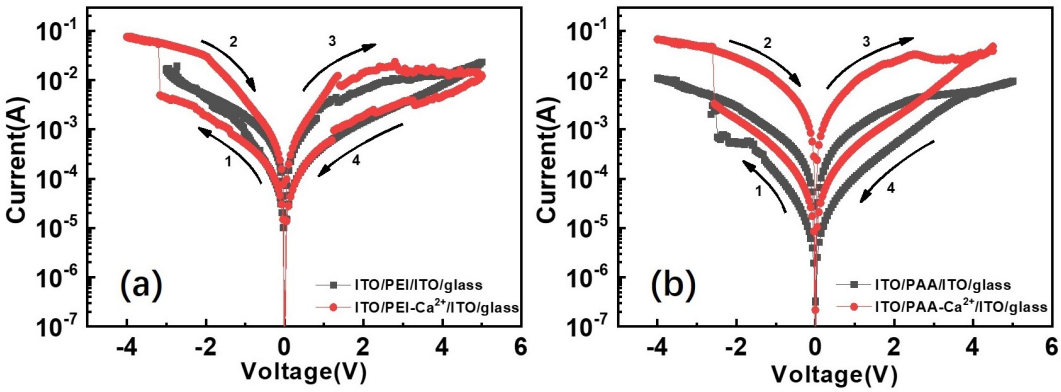

Figure S9. Pristine sweeps of (a) PEI and (b) PAA based devices (black line: without Ca^{2+} doping; red line: with Ca^{2+} doping).

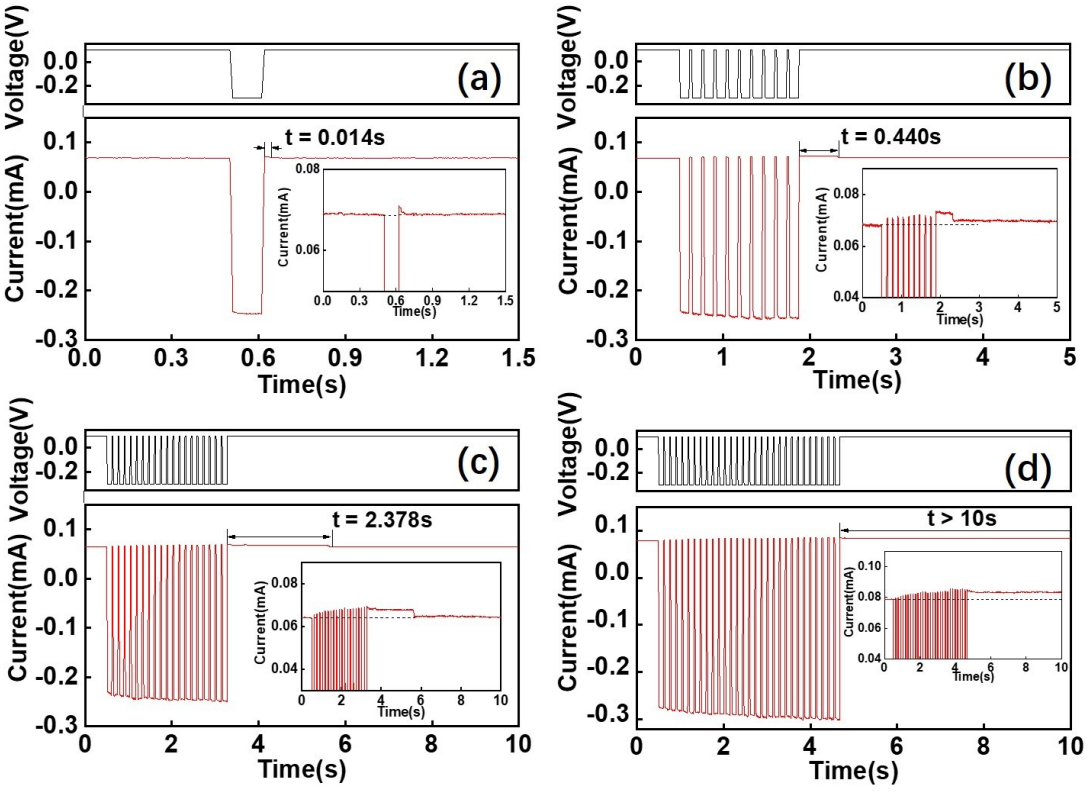

Figure S10. Synaptic plasticity with varied time scale manipulated by the number and rate of pulse. Device response to identical voltage pulses (-0.3V, 100ms) separated by a period of 20ms with different pulse numbers of 1, 10, 20 and 30 (a-d).

Additional Table

Table S1. XPS survey analysis of polyelectrolyte films with and without Calcium doping on ITO substrate.

Bare ITO	Bare ITO	PEI/ITO	PEI-Ca^{2+}/ITO	PAA/ITO	PAA-Ca^{2+}/ITO
C1s	54.6	73.9	63.5	62.1	65.4
N1s	1.6	11.4	6.0	2.1	1.5
O1s	30.8	12.8	15.8	31.4	24.1
Cl2p	0.8	0.6	8.6	0.9	2.8
Ca2p	1.8	1.1	5.4	0.6	5.0
In3d	9.3	0.2	0.7	2.1	1.2
Sn3d	1.1	0	0	0.8	0