Supporting Information

Oxygen Vacancies Migration/Diffusion Induced Synaptic Plasticity in a Single Titanate Nanobelt

Ming Xiao ^{a,b,c, #}, Daozhi Shen ^{a,d,e, #}, Kevin P. Musselman ^{a,b,c}, Walter W. Duley ^{a,e}, Y.

Norman Zhou ^{a,b,c*}

^a Centre for Advanced Materials Joining, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

^b Waterloo Institute of Nanotechnology, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

^c Department of Mechanics and Mechatronics Engineering, University of Waterloo, Ontario, N2L 3G1, Waterloo, Canada

^d Department of Mechanical Engineering, State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, P. R. China

^e Department of Physics and Astronomy, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

[#]These two authors contribute equally to this work.

*Corresponding author: Y. Norman Zhou, Centre for Advanced Materials Joining, Waterloo Institute of Nanotechnology, Department of Mechanics and Mechatronics Engineering, University of Waterloo, Ontario, N2L 3G1, Canada

Email address: nzhou@uwaterloo.ca



Figure S1. Comparison of contact geometry for nanowire vs. nanobelt. (a) Scanning TEM (STEM) image of a representative nanobelt and (b) its corresponding line-scan obtained from electron energy loss spectroscopy. This indicates that the nanobelt has a width of ~230 nm and a height of ~55 nm, with a width-to-height ratio of 4.2:1. These dimensions are consistent with a quasi-rectangular cross-section. (c) Schematic diagram showing the contact morphology at the Au electrodes for nanowire vs. nanobelt structures.



Figure S2. Current accumulation vs. number of identical consecutive 10 V pulses. The pulse duration, T, is as shown.



Figure S3. Evolution of the potentiation response on application of up to 2200 identical pulses. The pulse duration for each pulse is as indicated. Pulse amplitude is 10 V.



Figure S4. Potentiation and depression response. (a) 10 cycles of potentiation and depression response for 100 consecutive, 100 ms, +20 V pulses followed by 100 consecutive, 100 ms, -10

V pulses. A 2 V read voltage was applied after each pulse to obtain the current, (b) Expanded view of the area (A) in (a) demonstrating current potentiation. (c) Expanded view of the area (B) in (a) demonstrating current depression.



Figure S5. Potentiation/depression characteristics and current response for up to 50,000 pulses illustrating the robustness of the system and (b-f) demonstrated expanded view in selected region (B-F) in (a). P and D in (b-f) indicate potentiation and depression, respectively.



Figure S6. Current response for 2200 positive (+10 V) and negative (-6 V) pulses with identical durations of 100 ms, respectively.



Figure S7. Potentiation and quasi-depression response for different negative pulse amplitudes (a-c) 100 consecutive 20 V, 100 ms pulses followed by 100 consecutive -15 V, 100 ms pulses. (d-e) 100 consecutive 20 V 100 ms pulses followed by 100 consecutive -20 V, 100 ms pulses. All the pulses have a duty cycle of 50%. The current responses in (b) (c) (e) and (f) are extracted after each pulse at a 2 V read voltage.



Figure S8. Material characterization of Na₂Ti₃O₇ nanobelts. (a) SEM image, (b) TEM image, (c) HRTEM image (arrows point out defects in the crystalline structure), (d)Ti 2p XPS spectrum

(e) O1s XPS spectrum. The peak at 532.52 eV is attributed to oxygen vacancies (concentration ~ 25.00%), while the small shoulder at 535.3 eV is attributed to the OH- group in the Na₂Ti₃O₇ nanobelts (concentration ~ 8.12%). The strongest peak arises from oxygen in the lattice (concentration ~ 66.89%). (f) Na 1s XPS spectrum.



Figure S9. EPSC performance in a single Na₂Ti₃O₇ nanobelt device. (a) SEM image of the device. (b) EPSC response with a series of 12, 16, 18 and 20 V pulses 1000 ms long pulses. (c) The current response for different pulse amplitudes and calculated energy consumption. The calculated energy consumption is 630 pJ at a voltage of 12 V. (d) Summary of EPSC over more than 150 cycles with different pulse amplitudes. Variation in the current response for the 12 V pulse can be attributed to a low signal-to-noise ratio in the low current measurement.



Figure S10. Current accumulation and potentiation/depression response in a single $Na_2Ti_3O_7$ nanobelt device. (a) Current obtained under excitation with consecutive, identical, +20 V, 300 ms pulses. The total number of pulses is 75. (b) Potentiation and depression response over 5 cycles. Each cycle consists of 100 identical +20 V, 300 ms, pulses followed by 100 identical -10 V, 300 ms, pulses. (c) Detailed view for the selected region (A) for the current potentiation in (b). (d) Detailed view for the selected region (B) for the current depression in (b).



Figure S11. Spike rate-dependent synaptic plasticity of single $Na_2Ti_3O_7$ nanobelt devices under excitation with positive/negative pulses. (a) Evolution of current accumulation during 10 consecutive, +20 V, 400 ms, pulses, (b) current response vs. number of pulses with different positive pulse durations.



Figure S12. *I-V* curve for the electrical contact at the interfaces between Au electrodes and the $H_2Ti_3O_7$ nanobelt .



Figure S13. *I-V* curves for the volatile rectification behavior of single $H_2Ti_3O_7$ nanobelt device. The original *I-V* curve is obtained by sweeping from -5 to +5 V. The positive rectification curve is obtained by sweeping from -5 V to +5 V immediately after the positive sweeping from 0 to 10 V. Similarly, the negative rectification curve is obtained by sweeping from -5 V to +5 V immediately after the negative sweeping from 0 to -10 V. The sweeping speed is 50 mV s⁻¹.



Figure S14. Plot of $\ln(1/\tau)$ vs. 1000/T and linear fit from Equation 3 in main text for (a) single Na₂Ti₃O₇ and (b) single TiO₂ nanobelt devices from temperature dependence of current decay behavior following excitation with 100 consecutive +20 V, 500 ms, pulses. The calculated diffusion activation energy are E=0.41 eV and E=0.42 eV, respectively.