1. Introduction

The development of artificial neural networks that can emulate their biological counterparts is very promising and highly desired, especially in the era of Big Data.\cite{1,2} Compared to conventional digital computers designed according to the von Neumann configuration, in which the arithmetic/logic units and memory units are separated, the brain outperforms digital computers due to its dramatically different configuration, in which arithmetic calculation and memory operate simultaneously without the burden of data transmission. Hardware implementation of neuromorphic systems has attracted much interest due to the great potential inherent in machine learning at low power consumption. Conventional systems based on complementary metal-oxide semiconductor devices have been used for the emulation of synaptic behaviors,\cite{3,4} but these transistor devices bear little phenomenological similarity to the biological synapse\cite{5} and the realization of neuromorphic computing systems by traditional transistor devices requires the construction of large-scale parallel logic and switching cells. This is accompanied by high power consumption, complex structural configurations, and intrinsic difficulty in scaling down to meet the needs of future nanoelectronic devices. Solid state devices that can accurately emulate the functions and plasticity of biological synapses will be the most important basic building blocks in brain-inspired computation systems.\cite{6}
The memristor as a two-terminal device bears a striking resemblance to the biological synapse. Indeed, the resistance of a memristor is adjusted by the flow of charge through it, making the device ideal for mimicking the dynamics of biological synapses. Memristor is also more advantageous compared to transistors due to their simple structure, high switching speed, and easy integration into the networks required in the development of complex emergent behaviors. The functionality offered by a single memristor device can be used to replace up to 10 transistors on a chip, making it ideal for neuromorphic applications and for large-scale integration. Ion drift memristors have been widely studied as examples of systems that enable emulation of biological synapses. They exhibit a wide range of useful properties, including provision of a high number of resistance states, together with the ultrafast switching speeds that are important for neuromorphic computing applications such as pattern and face classification, and sparse coding. However, the non-volatile nature of these devices make them biologically unrealistic, which severely limit the realization of various synaptic functions. It has also been demonstrated theoretically that a second-order memristor, which takes into consideration both the conductance of the memristor device and its internal dynamics such as heat dissipation or mobility decay, is required to emulate the timing-controlled Ca\(^{2+}\) dynamics, including frequency-dependent plasticity and timing-based plasticity.

Recently, artificial synaptic devices based on volatile threshold switching, such as diffusive memristive devices, oxygen vacancy based devices, a graphene/MoS\(_2\) heterojunctions as well as bio-membrane based devices, are gaining increasing attention due to their resemblance of Ca\(^{2+}\) dynamics in biological synapses. In biological synapses, synaptic plasticity is regulated by Ca\(^{2+}\) dynamics and the information gathered by various sensory organs in the human body are transduced into electrical impulses, which are then processed by an elaborate and intricate network of neurons through the release of neurotransmitters within the human brain. The rise and subsequent spontaneous decay of Ca\(^{2+}\) concentration at the axon terminal caused by electrical neuronal stimuli (action potentials) regulates the release of these neurotransmitters into the synaptic cleft. During the release of the neurotransmitters, the Ca\(^{2+}\) gated channel will not open until the action potential is higher than a threshold value. When the integrated or total sum of the synaptic potential exceeds its threshold, the postsynaptic neuron will fire an action potential, that is, the neuron responds or conveys information to its connecting neurons and the process continues. After transmission, the subsequent spontaneous decay of ion concentration at the axon terminal returns the presynaptic neuron to its previous state. This process is at the root of information processing and memory in the brain. Thus, simulating the role of Ca\(^{2+}\) dynamics is key to the realization of bio-realistic artificial synapses. In volatile threshold switching devices, the abrupt change of current response that occurs upon exceeding a threshold voltage is also quite similar to the generation of action potential in the neurotransmission process. Spontaneous decay of the current response after applying the threshold voltage without the need for a reset circuit is similar to the decay of ion concentration after the release of neurotransmitter in a neuron. Relaxation to the original rest state after switching to the low resistance state provides an internal timing mechanism and allows the device to naturally emulate the rate- and timing-dependent synaptic effects in a bio-realistic fashion. Due to these advantages, the threshold switching behavior is highly suited to the emulation of brain activity in detecting the threshold level in a decision-making process. An example for the emulation would be the initiation of an escape from potential threats that involve an artificial nociceptor, which is a type of neuron that requires a certain threshold action potential for triggering an active response to pain stimulation.

Threshold switching devices for neuromorphic computing applications are normally based on the formation and dissolution of conductive filaments, including Ag filaments and nano-clusters and oxygen vacancies. It is found that by tuning the compliance current a transition from threshold switching to nonvolatile memory performance can be achieved due to the inherent thermal stability of the conductive filaments. However, the abrupt current-change nature of traditional threshold switching performance makes it unsuitable for potentiation and depression emulation of synaptic computation. This occurs because the relatively abrupt SET process for the filament formation in these threshold switching devices makes it difficult to implement gradual weight changes, as required in neuromorphic applications, where non-abrupt analog-like switching transitions and a wide dynamic range of conductance states are preferred.

In this work, we report that a fundamentally different threshold switching behavior can be achieved in a TiO\(_2\) nanobelt device. A symmetrical voltage-dependent capacitively-coupled threshold switching behavior is obtained, controlled by a transition from Schottky emission at low bias to trap assisted quantum tunneling at high bias. We also find that the presence of defects on the nanobelt is associated with a low activation energy for electron transport, together with dynamic charge trapping/detrapping, leading to a volatile threshold switching behavior instead of the nonvolatile performance observed in corresponding thin film devices. Significantly, the threshold switching performance of this new device facilitates the emulation of a nociceptor, including aspects of “threshold dynamics,” “relaxation,” “no adaptation,” “alldynia,” and “hyperalgesia” behavior. Via thermal admittance spectroscopy and temperature-dependent sweeping, the charge transport mechanism of the nanobelt device has been systematically studied. These results demonstrate that an individual nanobelt device can be utilized as a reliable building block for the realization of artificial sensory systems based on nanostructures grown with a bottom-to-top approach. This represents an essential milestone on the way to realizing nanowire-based artificial neural networks.

2. Results and Discussion

2.1. I–V Sweeping Performance and Transport Mechanism Study

Uniform TiO\(_2\) nanobelts were obtained via a hydrothermal process followed by thermal annealing at 700 °C for 2 h (Section 4). Typically, these nanobelts have a width of 50–200 nm, thickness of 15–50 nm and length in the range of...
5–20 μm, as shown in the scanning electron microscopy (SEM) image (Figure 1a). High-resolution transmission electron microscopy (HRTEM) characterization of one TiO$_2$ nanobelt confirms the single crystalline nature with a wide distribution of void defects as highlighted in Figure 1b. The oxygen 1s X-ray photoelectron spectroscopy (XPS) spectrum of the nanobelts shows the existence of defect oxygen peaks centered at 531.28 and 533.18 eV, corresponding to oxygen vacancies (20.25%) and hydroxide groups (7.98%), respectively (Figure 1c). Pt electrodes were fabricated via a standard photolithography process on a Si/SiO$_2$ wafer. The distance between adjacent electrodes is 2 μm (Figure 1d,e). Afterward, the diluted TiO$_2$ nanobelt solution was deposited on the electrodes. Individual nanobelts were located for further electrical characterization (Figure 1f).

Figure 2a,b shows the $I$–$V$ sweeping performance of the single TiO$_2$ nanobelt device on Pt-Pt electrodes at a constant sweep rate of 0.1 V s$^{-1}$ on linear and semi-logarithmic scales, respectively. A symmetrical hysteresis curve is observed in Figure 2a, implying resistive switching behavior. As shown in Figure 2b, when the voltage is less than 3 V, the device is initially in a highly insulating state with currents in the sub-pA range. At a higher voltage, the current response abruptly increases with the increase of electric field, changing from an insulating state (high resistance state [HRS]) to a voltage-dependent conductive state (low resistance state [LRS]). When sweeping back from 20 to 0 V, the current spontaneously relaxes to its baseline value as indicated by the arrows and numbers in both Figures 2a and 2b. This is a typical feature of volatile-switching behavior. The devices also demonstrate symmetrical behavior for the range of negative voltage sweeping, implying threshold-switching behavior for both polarities. This is significantly different from the nonvolatile memory behavior observed in the widely studied Pt-TiO$_2$ thin film-Pt sandwich devices, which can maintain their resistance states.\textsuperscript{[43–45]} In contrast to most other reported threshold switching behaviors based on the filament formation and rupture of Ag ions\textsuperscript{[27–31]} or oxygen vacancies,\textsuperscript{[34–36]} the present TiO$_2$ nanobelt devices demonstrate a threshold-switching performance without the need for a compliance current, as normally required for filament-based threshold-switching devices in both/either SET or RESET processes to avoid permanent breakdown. This helps to avoid some limitations imposed on the scaling down of these devices, as integration of other electronic components such as a transistor are normally required to restrict the working current in this type of configuration.\textsuperscript{[46]} The continuous current change above the threshold voltage for the TiO$_2$ nanobelt device, which can facilitate the adjustable weight changes desired in neuromorphic computing, also implies that the mechanism is different from abrupt filament formation and rupture observed in other reported threshold-switching devices.

The single nanobelt device shows reproducible performance with a resistance ratio up to $1.3 \times 10^4$ for a sweeping range of 20 V (Figure 2c). This LRS/HRS ratio is dependent on the sweeping voltage, as shown in Figure 2d, which could provide potential for the precise resistance state to be tuned by the applied electric field. A statistical summary of 26 devices with identical geometry fabricated on a single chip was obtained and the results showed a logarithmic normal distribution of the resistance ratio (Figure 2e). The device-to-device variation could be attributed to the difference between contact areas of individual nanobelts on the electrodes. The as-fabricated TiO$_2$ nanobelt devices are further characterized by a highly repeatable and symmetrical switching behavior when excited with bipolar pulses over 10000 cycles. This shows that these devices are highly robust (Figure 2f). Devices that do not have a TiO$_2$ nanobelt bridging the Pt electrodes only have insulating capacitive
characteristics, which excludes the threshold switching behavior originating from the SiO₂ substrate (Figure S1, Supporting Information).

To further explore this threshold switching behavior, the sweeping performance under different voltages at a constant sweep rate of 0.1 V s⁻¹ has been evaluated as shown in Figure 3. The full range of sweeping behavior can be found in Figures S2 and S3 (Supporting Information). It can be seen that, at a small sweeping bias such as 2 V, the single nanobelt device responds with the charging and discharging cyclic voltammetry curves of a capacitor with a parallel resistor (Figure 3a,d). This characteristic likely arises due to the Schottky barrier created between the electrode and the nanobelt. When the bias exceeds 3 V, the device exhibits a symmetric resistive switching behavior, which is evident from the capacitive contribution from low bias. The inset of each figure shows the equivalent circuit of the devices at different sweeping voltages.

Figure 2. Threshold switching sweeping performance for single TiO₂ nanobelt devices. a) Sweeping performance at 20 V at a constant sweeping rate of 0.1 V s⁻¹ plotted on a linear scale, b) corresponding I–V curve plotted on a semi-logarithmic scale. c) LRS/HRS ratio for the device at a reading voltage of 3 V over 80 sweeping cycles in (b). d) Sweeping voltage dependent performance and summary of LRS/HRS ratio at the reading voltage of 3 V. e) Statistical summary for the LRS/HRS ratio among 26 devices having identical geometries. f) Endurance performance for 10 000 cycles at room temperature. The inset shows one cycle of the applied pulses, where the 2 V, 50 ms and −2 V, 50 ms pulses are used as read pulses. The device did not fail during the measurement, showing a high degree of robustness.

Figure 3. I–V sweeping performance for the single TiO₂ nanobelt device at different sweeping voltages. At a low sweeping range such as 2 V ((a) and (d)), the device demonstrates the typical charging and discharging cyclic voltammetry curves of a capacitor with a parallel resistor. However, at higher bias such as 6 V ((b) and (e)) and 10 V ((c) and (f)), a volatile threshold switching performance is observed, including the capacitive contribution from low bias. The inset of each figure shows the equivalent circuit of the devices at different sweeping voltages.
performance at high bias while the contribution of the capacitive response remained at low bias (Figure 3b,e and Figures S1c and S2c, Supporting Information). This implies that the single TiO2 nanobelt device changes from a capacitive behavior to a capacitive-coupled memristor behavior when the sweeping bias exceeds 3 V. The capacitive-coupled memristive effect has been previously reported in the case of nonvolatile memory devices,[47] but, to the best of our knowledge, this is the first time that this characteristic has been reported in volatile threshold switching devices.[48] Further increasing the sweeping bias up to 10 V (Figure 3c,f) and 20 V (Figures S2i and S3i, Supporting Information) will lead to an increased current for the resistive switching behavior, but the devices still have a small capacitive contribution at low bias. This is why the I–V curve of the TiO2 nanobelt device is not pinched to zero, in great contrast to the zero-crossing behavior typically observed in memristive devices. This property is unique and is quite different from the characteristics of other threshold switching devices, in which the filament formation and rupture leads to memristive behavior with a zero-crossing feature and abrupt change between resistance states.

The high aspect ratio of the nanobelt implies that the performance of the single nanobelt device can be susceptible to the presence of surface trapping sites.[49] This would result in an I–V behavior that could be independent of the electrodes. To test this possibility, we fabricated single TiO2 nanobelt devices on different electrodes. As shown in Figure S4, Supporting Information, the devices constructed with Au-Au and Ti-Ti electrodes both demonstrated similar volatile threshold-switching characteristics, differing only in current amplitude compared to the device using Pt-Pt electrodes. With Ti electrodes, the theoretical difference between the Ti work function (4.33 eV) and the TiO2 Fermi level (4.2 eV) is small enough to lead to an Ohmic contact. Nevertheless, the sweeping performance is similar to that observed for the Pt and Au electrodes, indicating that at least, partial Fermi level pinning[50–55] may be occurring due to the surface-dominating nature of the TiO2 nanobelts. A similar transition from a capacitive behavior to a capacitive-coupled memristive behavior is observed for the device with Au-Au electrodes (Figure S5, Supporting Information).

It should be noted that the defects in the TiO2 nanobelts are critical for obtaining a resistive switching response.[56] We tested this by further annealing the as-synthesized TiO2 nanobelts for 2 h at 700 °C prior to device fabrication. Nanobelts subject to this treatment are almost perfectly single-crystalline as evident from HRTEM (Figure S6a,b, Supporting Information). However, such devices exist in a highly insulating capacitive state up to a sweeping voltage of 40 V (Figure S6c, Supporting Information).

To study the charge transport behavior of these TiO2 nanobelt devices, the I–V sweeping performance is examined at different temperatures, as shown in Figure 4. With increasing temperatures, the current response increases significantly, implying a temperature-related charge transport mechanism in the single TiO2 nanobelt devices (Figure 4a). Due to the symmetrical behavior of the current response, only the current under forward voltages is fitted with possible charge transport equations at different stages that are divided by threshold voltage, $V_\text{th}$. In Stage I, the linear slope dependence of ln($J/T^2$) with $1/T$ implies the introduction of a Schottky barrier. The typical Schottky emission equation is expressed as[57]

$$J = A^* T^\frac{3}{2} \exp \left[ -\frac{q(\varphi_B - \frac{\sqrt{2m^*e}}{4\pi\varepsilon\varepsilon_0}E)}{kT} \right]$$

(1)

where, $J$ is the current density, $A^*$ is the effective Richardson constant in the dielectric material, $q$ is electron charge, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $E$ is the electric field, $\varphi_B$ is the barrier height, $\varepsilon_i$ is the optical dielectric constant, and $\varepsilon_0$ is the permittivity of the dielectric material in vacuum. From this equation, a plot of ln($J/T^2$) versus $1/T$ at different voltages and ln($J/T^2$) versus $E^{1/2}$ at different temperatures should be linear, as confirmed in Figure 4b and Figure S7a,c, Supporting Information. In Stage I, an effective Schottky barrier must be formed at the interface between the Pt electrodes and the TiO2 nanobelt layer. An effective Schottky barrier height of $\varphi_B = 0.80 \pm 0.04$ eV is obtained from the intercept of the ln($J/T^2$)-$E^{1/2}$ curve. This barrier is smaller than the theoretical barrier (1.2 eV) obtained from the difference between the Pt work function (5.2 eV) and the TiO2 electron affinity (4.0 eV).[58] The lower effective Schottky barrier obtained from the fit could be due to the existence of electron traps at surface defects that promote the injected electron transfer from the electrode. This phenomenon has been widely explored in one dimensional (1D) semiconductor nanomaterial-based devices.[49,59–61]

Furthermore, due to the highly defective nature of the TiO2 nanobelts, oxygen vacancies or hydroxide groups on the surface function as localized charge-carrier centers providing paths for injected electrons to hop from one localized site to another when an external electric field is applied. At low electric field in Stage I, the temperature dependence of the resistance of the TiO2 nanobelt device can be described using a Mott-variable range hopping (VRH) conduction mechanism according to the equation[62]

$$R = R_0 \exp \left( \left( \frac{T}{T_0} \right)^\frac{1}{3} \right)$$

(2)

where $T_0$ and $R_0$ are constants determined by the material. From this equation, the device resistance, ln($R$), is proportional to $1/T^{1/4}$, as evident in Figure 4c. This suggests that the injected electrons from the electrode can hop to a range of different localized states at the Pt/TiO2 interface, where a high concentration of defects is present.

At Stage II, the current response is best fitted with the trap-assisted tunneling (TAT) equation[63]

$$J = A \exp \left( -\frac{8\pi \sqrt{2m^*e}}{3hE} \varphi_T^{1/2} \right)$$

(3)

where, $A$ is a constant, $\varphi_T$ is the trap energy level with respect to the conduction band edge of the oxide, $m^*$ is the electron effective mass in the dielectric material, and $h$ is Planck’s constant. We use $m^* = 1.0 \ m_0$ (where $m_0$ is the mass of an electron) as an estimate of the trap energy level in our device.[64,65] From
Equation (3), we obtain a linear relationship between $\ln(J)$ and $1/E$ with a slope dependent on the effective trap energy level, $\Phi_T$, as given in Figure 4d. The derived trap energy level is $\Phi_{T-II} = 35.3 \pm 2.7$ meV for Stage II. Trap-assisted tunneling typically occurs when the electrons tunnel through a thin highly defective dielectric layer promoted by defects. In the present system, the surface defects at the Pt-TiO$_2$ interface are likely to function as trap centers that promote injected electron tunneling from the electrode to the conduction band of the TiO$_2$ nanobelt. Schottky emission effect in this stage can be excluded as the fit to the relationship between $\ln(J/T^2)$ versus $(1/T)$ is not linear (Figure S7a, Supporting Information). A contribution from Fowler–Nordheim tunneling is also possible (Figure S8a, Supporting Information), but the main conduction mechanism must arise from TAT due to the higher probability for electron trapping compared to that for tunneling through the Pt/TiO$_2$ interface.

The properties of the trapping states in the TiO$_2$ nanobelt device have also been examined using thermal admittance spectroscopy. The technique consists of calculating the derivative of the junction capacitance with respect to the angular frequency of the small voltage perturbation (50 mV) applied...
to the devices at different temperatures. Defect states within the bandgap contribute to the junction capacitance depending on their energy and spatial location. For the present device, in the transition from low to high frequency, a step capacitance accompanied by a loss peak is observed near the frequency $v_{\text{max}}$ (Figure S9a,b, Supporting Information). Analysis of these data yields an activation energy $A\varepsilon$ of $38 \pm 2$ meV and an attempt-to-escape frequency of $2.6 \times 10^4$ s$^{-1}$ at 300 K (Figure S9c, Supporting Information). The activation energy $A\varepsilon$ is defined as the difference between the defect state energy $E_T$ and the conduction band energy $E_C$ for electron traps as $A\varepsilon = E_C - E_T$ or the difference between the defect state energy $E_T$ and valence band energy $E_V$ as $A\varepsilon = E_T - E_V$ for hole traps, respectively. In the present devices, only the electron traps are considered due to the N-type semiconductor nature for TiO$_2$.[67,68] however, it is in the same range as that observed for the TAT fit for Stage II, suggesting that surface defects are critical in determining the charge transport behavior of the TiO$_2$ nanobelt devices. The density of states (DOS) can also be obtained as shown in Figure S9d, Supporting Information, and shows a Gaussian peak centered at the fitted activation energy at different temperatures with a full width at half maximum of 34 meV at 300 K.

The TAT equation also applies in the high voltage range in Stage III in the low resistance state. Here, the data gives a much smaller slope for the fitted equation (Figure 4e). The trap energy level derived from this fit is $\varepsilon_{T\text{-III}} = 14.7 \pm 0.5$ meV for Stage III. This suggests that the hysteresis behavior is probably due to the difference in the effective trap energy. When sweeping from 0 to 10 V, TAT occurs and some of the traps are occupied by charge trapping, leading to the reduction of number of TAT paths. On sweeping back from 10 to 0 V, traps in deeper levels might already be filled and some shallower traps could be involved in the charge transport mechanism, leading to a shallower derived trap energy. Filling of deep trap states will also lead to an upward shift of the Fermi level ($E_F$), rendering shallow trap states closer to the $E_F$ in Stage III.[69,70]

Thus, it is suggested that from Stage II to Stage III, this nonequilibrium trapping dynamics by the defect states of the TiO$_2$ nanobelts causes the difference in the current response from the same trap-assisted tunneling mechanism, leading to observed hysteresis in current.[49] that is, resistive switching behavior. This assumption is supported by the sweeping voltage dependent hysteresis behavior shown in Figure 2d,3 and Figures S2 and S3, Supporting Information. The application of a larger electric field allows further trapping of electrons by available trap states, correspondingly increasing the hysteresis effect and therefore resulting in a higher LRS/HRS ratio. This nonequilibrium dynamic trapping behavior is further supported by sweeping-rate I–V performance of the device, as shown in Figure S10, Supporting Information, where a higher sweeping rate leads to a decrease of the hysteresis effect due to the limited timescale for charge trapping. During this stage, the effect of Schottky emission and Fowler–Nordheim tunneling can be excluded since the I–V performance did not fit with the corresponding equations (Figures S7b and S8b, Supporting Information).

In Stage IV, the I–V response can be fit with the Schottky emission equation, as shown in Figure 4f and Figure S7d, Supporting Information. At this stage, the effective Schottky barrier is estimated to be $\varepsilon_{B\text{-IV}} = 0.67 \pm 0.03$ eV. The lower Schottky barrier in Stage IV compared to Stage I can be attributed to the upward shift of $E_F$ due to electron trapping from Stage II to Stage III which results in the lowering of the upward band bending at the Pt/TiO$_2$ interface.

Overall, it is proposed that the switching mechanism of the single TiO$_2$ nanobelt device can be described by dynamic nonequilibrium charge trapping process that modulate the Schottky barrier profile as well as the trap-assisted quantum tunneling process. The existence of defects in TiO$_2$ nanobelts causes tailoring of the DOS compared to that of pure TiO$_2$ (Figure 4g).[71] Many of these available trap sites at the Pt/TiO$_2$ interface are likely empty initially, which makes the pristine device remain in HRS due to the Schottky barrier at zero bias (Figure 4h). In this regime, charge transport is dominated by Schottky emission at low forward electric field in Stage I (Figure 4i) and hopping of electrons to various localized trap sites occurs. When a sufficiently high positive voltage is applied to the electrode causing the trap level to be pulled down to below the Fermi energy level, the trap sites start to be filled by electron injection from the Pt electrode. The available trap states at the Pt/TiO$_2$ interface leads to a defect promoted (or trap-assisted) tunneling response in Stage II (Figure 4j). Meanwhile, the dynamic electron trapping causes the modulation of trap-assisted tunneling process, leading to the hysteresis response in Stage III (Figure 4k). The accumulated electron trapping under applied electric field could possibly cause the effective Schottky barrier to be lowered in Stage IV, in which the spontaneous charge detrapping occurred, making the device return to the initial state (Figure 4l). Redox reactions may also be involved in the resistive switching process in single TiO$_2$ nanobelt device, but are not considered as the primary mechanism since redox reactions based on atmospheres O$_2$ molecules would lead to a modulation of the effective Schottky barrier strength. This is not an important effect due to the dominance of the TAT mechanism in Stages II and III.

### 2.2. Artificial Nociceptor Emulation

Previously, we demonstrated that the devices based on a single titanate nanobelt could be used for emulation of key features of a biological synapse, including excitatory postsynaptic current (EPSC), paired pulse facilitation, short-term plasticity, potentiation, and depression.[42] As a continuation of this work, we show that such threshold switching performance in a single TiO$_2$ nanobelt device can be used for the emulation of an artificial nociceptor.[24–26,72] A nociceptor is a critical and special sensory neuron receptor whose role is to detect a variety of noxious stimuli generated by different types of stimuli such as mechanical, thermal, electrical, and optical. The response of the nociceptor is to rapidly transmit pain signals to the central nervous system to initiate a motor response in the human body to avoid potential damage to the organism. It not only possesses the threshold switching and relaxation dynamics that occur for neurotransmission in normal neurons when exposed to noxious
stimuli, but also demonstrates its characteristic features such as “no adaptation,” “allodynia,” and “hyperalgesia” upon repeated stimuli and excessive intensive stimuli, respectively.

Figure 5a is a schematic diagram of the neuron transmission process in a nociceptor. Various types of noxious stimuli that are detected at the periphery terminal can activate the receptor complexes via a receptor potential to initiate an action potential that will be transmitted along the length of axons to the dorsal horn of the spinal cord.\cite{73,74}

When a defined depolarization threshold for the presynaptic membrane is reached, voltage-gated sodium channels are activated, and an action potential is generated. Afterward, potassium channels are opened to repolarize the presynaptic membrane, leading to the closing of the sodium channel gate. This will allow the sodium channel to return to a closed resting. An action potential travels along the axon to the presynaptic terminals, triggering the release of neurotransmitters to the postsynaptic terminal in the spinal cord through the voltage-gated calcium channels.

Similarly, in the threshold switching devices, the devices will not be switched to the conductive state if the input voltage is below a certain value (Figure 5b). In our TiO\textsubscript{2} nanobelt device, the threshold voltage determines the electric field that leads to the trapping of injected electrons. For voltages less than this value, only passive resistance occurs. Upon removal of the voltage, a relaxation process returns the TiO\textsubscript{2} nanobelt device to its initial state due to the spontaneous detrapping process, similar to the process when action potential returns to the resting state in the nociceptor. In the neuron transmission in a nociceptor, the triggering of the action potential is highly dependent on the intensity, duration, and the number of stimuli. To simulate this property, we used different numbers of electrical pulses having various amplitudes and pulse width. We set the threshold current as $1 \times 10^{-10}$ A, below which the stimuli is not considered as effective for the artificial nociceptor. With a single electrical pulse of 50 ms width, the device was found not to be switched on until the pulse amplitude reached 6 V. Further increase of the amplitude to 10 V resulted in a larger output current (Figure 5c). This is consistent with the increase of response intensity corresponding to a higher concentration of Na\textsuperscript{+} and Ca\textsuperscript{2+} residue leading to a larger action potential in

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Figure 5. Threshold dynamics of the single TiO\textsubscript{2} nanobelt devices emulating a nociceptor. a) Schematic of neuron transmission for a nociceptor. b) Schematic diagram for threshold switching in the device. The threshold value will determine the output current response, below which no or insignificant current response is detected. c) Response of the single TiO\textsubscript{2} nanobelt device to single 50 ms pulses with different amplitudes from 3 to 10 V. d) Response of the single TiO\textsubscript{2} nanobelt device to number of 50 ms pulses at various pulse amplitudes.
the nociceptor. As to the effect of pulse number, different numbers of 50 ms pulses with amplitudes of 4, 4.5, and 5 V were applied. It was shown that a much higher number of pulses (20 pulses) is needed for the 4 V pulse to reach the threshold current value compared to the 5 V pulse (4 pulses) (Figure 5d). With a fixed pulse amplitude (in this case 5 V), we observed that a sufficiently long pulse width (400 ms) was necessary to reach the threshold value for the device and a further increase in pulse length led to a larger output current (Figure S11, Supporting Information).

Other different characteristics of a nociceptor have been evaluated for the TiO$_2$ nanobelt devices, as shown in Figure 6. As revealed in the charge transport mechanism study, defect centers in the TiO$_2$ nanobelt function as electron traps. Therefore, with the applied bias, it is expected that the increase in the conductivity of the nanobelt device upon application of pulses will gradually slow down (as more traps are filled) until it reaches saturation, indicating a dynamic equilibrium is achieved under repeated stimuli. To test this hypothesis, a number of pulse amplitudes of 10, 15, and 20 V were applied to the devices and the resulting current response is shown in Figure 6a. The generated current increases gradually after each pulse, suggesting that electrons injected by the applied pulses are gradually filling the available trap states and in turn facilitating smoother conduction for subsequent pulses. It was also observed that the current increases until saturation, indicating that the present devices can be used for the emulation of the “no adaptation” feature of nociceptors, in which the neuron will not adapt to further repeated noxious stimuli as the sensitivity of the nociceptor gradually reduces upon exposure to external stimuli for a prolonged time. Pulses with higher amplitude yield a higher saturation current. Saturation may occur due to an equilibrium between the trap-filling rate determined by the electrical field and the spontaneously occurring trap-emptying rate. In this case, more trap states will be filled at equilibrium when the pulse amplitude is higher (larger electric field), such that conduction will be facilitated and the saturation current is higher.

After the stimuli are removed, the nociceptor starts the relaxation process and finally recovers its initial state. This relaxation behavior is examined in the single TiO$_2$ nanobelt device by applying a single pulse and recording the transient current at a reading voltage. As can be seen in Figure 6b, a single 50 ms 10 V pulse leads to an EPSC. The transient current recorded at 2 V reading voltage shows relaxation to the original high-resistance state after a defined period. This response is similar to the relaxation behavior in nociceptors, whereby the neuron relaxes back to the initial state upon the removal of the noxious stimuli. During this time, detrapping of electrons from defects in the TiO$_2$ nanobelts could recover the initial high resistance state with a Schottky barrier at the Pt/TiO$_2$ interface, that is, the relaxation of the LRS to the initial state. A fit to the temperature-dependent current relaxation curves yields an activation energy of 0.27 eV. This can be associated with the activation energy for the release of electrons from trap centers (Figure 6c).

We have also studied the relaxation behavior when single 50 ms pulses...
6, 7, and 8 V pulses were applied (Figure S12a–c, Supporting Information). The results show that the relaxation time can be shortened when smaller amplitude pulses are applied. Further decreasing the pulse amplitude to 4 V (Figure S12d, Supporting Information) only causes a passive resistance behavior and no current relaxation can be detected.

These results indicate that the relaxation behavior is dominated by the detrapping process for electrons. This process is directly related to the concentration of oxygen vacancies in the nanobelts. Engineering the oxygen vacancy concentration in the TiO$_2$ nanobelts was then considered as a possible method for adjusting the relaxation time. As it is well-known, exposure to laser irradiation can generate oxygen vacancies in metal oxide materials.[75] To implement this adjustment, femtosecond (fs) laser irradiation was used to increase the oxygen vacancy concentration in the solution containing TiO$_2$ nanobelts. Fabrication using standard methodology following irradiation of TiO$_2$ nanobelts solution then results in single TiO$_2$ nanobelt devices with a wide range of oxygen vacancy concentration. The XPS data shows that oxygen vacancy concentration continues to increase with laser irradiation up to 15 min at a fluence of 23 mJ cm$^{-2}$ (Figure S13a,d,g, Supporting Information). The corresponding $I$–V sweeping performance for different irradiation periods is shown in Figure S13b,e,h, Supporting Information. We can see that a similar threshold switching behavior is obtained in each case, only differing current amplitude when compared to that seen in un-irradiated TiO$_2$ nanobelt. Relaxation behavior for these devices was studied by applying a single 50 ms 10 V pulse and recording the transient (Figure S13c,f,i, Supporting Information). It is apparent that the relaxation time decreases after laser irradiation. Measured time constants derived from a fit with a single exponential decay equation are 33.52, 25.04, and 13.36 s, for irradiation lasting for 5, 10, and 15 min, respectively. These are all smaller than the time constant for the TiO$_2$ nanobelt device without any laser treatment, 52.35 s. This shows that engineering the concentration of oxygen vacancies in the TiO$_2$ nanobelts by exposure to fs laser irradiation results in a substantial decrease in relaxation time.

The injured state for a nociceptor typically occurs when enough intense stimuli are applied to damage the nociceptor. A nociceptor will show an enhanced response at a reduced threshold after injury, known as “allodynia” and “hyperalgesia.” This is illustrated schematically in Figure 6d.[24–26] To demonstrate the allodynia and hyperalgesia properties, a pulse with a relatively high amplitude (15 and 20 V) is used to generate an injured condition. The measured current response at an injured condition and an uninjured condition as a function of applied voltage is shown in Figure 6e. Before the application of the 20 V 50 ms pulse on the TiO$_2$ nanobelt device, the “uninjured” nociceptor device initially has low current responses. This changes significantly in the “injured” nociceptor device. The injured nociceptor devices have a higher output current response, while the threshold voltage shifts to lower values. This demonstrates that a smaller threshold voltage is required to switch on a more seriously injured device, successfully emulating the “allodynia” and “hyperalgesia” properties of a nociceptor. To reveal the variation of this response with time, a sequence of input pulses was applied at different interval times after the application of the injury pulse (Figure 6f). We can see that as the time interval increased, the current response to the input pulse decreases and is expected to relaxed to the initial state when the device is not damaged, revealing the relaxation and recovery property over time for the nociceptor, as previously outlined in Figure 6b,c. Similarly, the TiO$_2$ nanobelt device demonstrated “allodynia” and “hyperalgesia” behavior under different time intervals. This can be attributed to the fact that the original, high-amplitude pulse partly fills up the traps resulting in an increase in the conductivity of the device. Before it relaxes to the initial state due to the charge detrapping processes, further application of pulses would result in an enhanced current response as well as the threshold value being reached at lower pulse amplitude. Furthermore, detrapping of electrons after the application of the pulses is a spontaneous process resulting in a gradual relaxation over time, suggesting that “injured” nociceptor devices can eventually recover from the injured state. It is evident from the above analysis that all five features of a nociceptor, notably “threshold,” “relaxation,” “no adaptation,” “allodynia,” and “hyperalgesia” can be realized in a single TiO$_2$ nanobelt device.

3. Conclusion

We have presented a unique threshold switching behavior based on a single TiO$_2$ nanobelt device. Current flows in the TiO$_2$ nanobelt device in response to a Schottky limited process at low bias to defect assisted quantum tunneling process at high bias, together with dynamic charge trapping/detrapping with shallow trap energy levels at different stages. As a result, a volatile voltage-dependent threshold switching performance is obtained and is used to mimic all key features of a nociceptor, including “threshold,” “relaxation,” “no adaptation,” “allodynia,” and “hyperalgesia.” These results demonstrate that a single 1D metal oxide nanomaterial can be used as a building block for the realization of artificial receptor devices in place of complex circuits, paving the way for the realization of nanowire- or nanobelt-based artificial neural networks via a bottom-up approach.

4. Experimental Section

$\text{TiO}_2$ Nanobelt Synthesis: TiO$_2$ nanobelts were synthesized via a hydrothermal process from TiO$_2$ nanoparticles.[42] Typically, 0.75 g commercial TiO$_2$ nanoparticles, P25 (Sigma Aldrich, Canada), was dissolved in 10 M sodium hydroxide alkaline solution (60 mL) and then was poured into a Teflon-lined stainless-steel autoclave (capacity: 125 mL, Parr Instruments). The autoclave was kept in a furnace at a temperature of 250 °C for 24 h. The suspended nanobelts were taken out from the autoclave after being cooled down naturally and were washed with ultrapure water. The obtained nanobelts were immersed in 0.1 M HCl solution for 12 h for ionic exchange. Afterward, the solution was filtered and the obtained residues were then dried in a furnace at 80 °C for 8 h to obtain the nanobelt powders. Finally, the obtained powder was annealed at 700 °C for 2 h to obtain the anatase TiO$_2$ nanobelts. For the device fabrication, the TiO$_2$ nanobelts were harvested by sonication of 0.5 mg in pure acetone solution before the device fabrication.

Device Fabrication: Pt electrodes were fabricated on a SiO$_2$/Si substrate with standard photolithography and lift-off process. To fabricate the TiO$_2$ nanobelt device, electrodes were first rinsed with...
acetonitrile, isopropanol, and ultrapure water, respectively, and dried with flowing nitrogen gas. The devices were treated in an oxygen plasma machine (Tergeo Series, PIE Scientific) at a power of 75 W for 40 s to lead to a hydrophilic nature of the surface of the electrode. Diluted solution of TiO$_2$ nanobelts were then drop-cast on Pt electrodes and the device was baked at 100 °C for 30 min on a hot plate to fully evaporate the solvent. Samples with bridged TiO$_2$ nanobelt on the electrodes were located using optical microscopy before electrical characterization. To ensure good interconnection between the Pt electrodes and the TiO$_2$ nanobelt, only devices in which both ends were fully contacted with the electrodes were selected. This means that the contact areas at both ends of the nanobelt were similar.

Characterization: The morphology and device of TiO$_2$ nanobelts were characterized by SEM (LEO 1530). Oxygen chemical states of the nanobelt were similar. The electrodes were selected. This means that the contact areas at both ends of the nanowire were similar.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
artificial synapses, charge trapping/detrapping, nanodevices, noncoercive, threshold switching

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