Memristors are deemed to be the electrical twin to biological synapses. They enable emulation of human memory functionalities such as learning, memorizing, and forgetting. The present hydrothermally grown titanium dioxide nanowire array memristive devices have shown to be able to mimic synaptic behaviors. As well as spike-rate dependent plasticity, excitatory postsynaptic currents, and paired pulse facilitation, high endurance, and on/off ratios for the nanowire arrays are presented. Decay fitting of postsynaptic currents with Kohlrausch’s equation shows lifetimes of few milliseconds up to several hundred seconds, offering the possibility of a short-term to long-term memory transition. Furthermore, a strong dependence of the lifetime of the signals on the frequency and amplitude of the stimulation pulses is observed.

1. Introduction

An understanding of complex human brain functionalities becomes more and more important to approach neuromorphic computing systems.[3–3] Many human brain mechanisms are already understood quite well, whereas human learning and forgetting are related to synapses.[4,5] A synapse is the connection between two neurons and is responsible for the signal transfer between them. In the first neuron an action potential along the membrane is sent to the endings of the neuron, the presynaptic region. The increased potential leads to an opening of Calcium-membrane is sent to the endings of the neuron, the presynaptic region. In the first neuron an action potential along the membrane is sent to the endings of the neuron, the presynaptic region. In the first neuron an action potential along the membrane is sent to the endings of the neuron, the presynaptic region. In the first neuron an action potential along the membrane is sent to the endings of the neuron, the presynaptic region.

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2. Results and Discussion

The hydrothermally grown nanorod arrays (Figure 1a) are investigated using a simple two electrode system, shown in Figure 1b (inset). The FTO substrate is used as bottom electrode, whereas a gold tip contacts the nanowires from the top. Since multiple nanowires are contacted by this method, they act as parallel resistors. The current–voltage (I–V) characteristics are shown in Figure 1b on a logarithmic scale.

The curve shows an asymmetric behavior with a higher conductivity for a negative applied potential. In a previous work, we showed that the asymmetry results from the asymmetry of the nanowires itself.[13] The difference in the resistance can be clearly seen at a voltage of 0.1 V. Therefore, the read-out and
Itoxygen vacancies at either the top or bottom of the nanowire, memristors could similarly be attributed to an accumulation of consisting of n-type dopants like oxygen vacancies.[32–34] The related to an accumulation and/or formation of filaments onstrated even earlier.[35] Due to the asymmetry of the nanowires, the redistribution of the oxygen vacancies in TiO$_x$ is most likely related to an accumulation and/or formation of filaments consisting of n-type dopants like oxygen vacancies.[32–34] The long-term behavior of the LRS and the IRS of TiO$_x$ nanorod memristors could similarly be attributed to an accumulation of oxygen vacancies at either the top or bottom of the nanowire, dependent on the applied polarity.[34] A retention loss after several minutes has been related to a redistribution of oxygen vacancies following a concentration gradient, which was demonstrated even earlier.[35] Due to the asymmetry of the nanowires, the redistribution of the oxygen vacancies happens on different timescales for the two polarities. These observations are now used to explain the following synaptic functionalities of hydrothermally grown TiO$_x$ memristors. Endurance measurements over 1000 cycles are shown in Figure 1c. The conductivity of both states increases within the first 10–50 cycles, followed by a quite stabilized value for both the LRS and the IRS. Within the first cycles, the amount of accumulated oxygen vacancies at each electrode increases, lowering the interface barrier and hence, leading to a higher conductivity. The redistribution is slower than the cycling speed, so that the amount of accumulated vacancies increases per cycle. Slower cycling speeds lead to similar $I$–$V$ characteristics, since the redistribution also takes longer. At some point, an equilibrium between the two competing effects, the redistribution versus the accumulation due to the electric field of the next cycle, is reached and resistance states stabilize.

The spike-rate dependent plasticity (SRDP) is shown in Figure 2a for a negative applied potential, as well as a positive potential in Figure 2b (further frequencies can be seen in Figure S1, Supporting Information). Ten voltage pulses of 1 s duration at frequencies of 0.17 to 0.67 Hz are applied to the memristors (see schematic in Figure 3a). The excitatory postsynaptic current (EPSC) between each pulse is recorded at 0.1 V. An example for the EPSC for both polarities is given in Figure 2c,d for a frequency of 0.25 Hz. After each pulse train (one pulse train contains 10 voltage pulses) the transient current is recorded at 0.1 V for 60 s, so that the device can relax back to equilibrium. For a stimulation amplitude of 3.3 V and frequencies >0.25 Hz, the 60 s are too short to let the device relax back to the HRS, so that the current of the first voltage pulse of the next pulse train is already higher than the current height of the very first voltage pulse. This indicates already the possibility of a short-term to long-term memory transition for short pulse intervals and large voltage amplitudes. The EPSC decay for a negative applied potential perfectly follows a single stretched exponential decay (Kohlrausch’s law$^{[36–39]}$)

$$I(t) = I_0 \cdot K \cdot \exp\left(-\frac{t}{\tau}\right)^\beta$$

(1)

see fit in Figure 2c. $I_{0,K}$ is the thereby the amplitude, $\tau$ is the lifetime of the decay process, and $\beta$ the stretching factor of the exponential decay. The Kohlrausch relaxation is based on a stochastic nature of relaxation processes$^{[36,40,41]}$ and is mostly used for relaxation processes based on oxygen redistribution.$^{[17,42–44]}$ This fits very well to our findings in a previous work$^{[33]}$ where the retention loss could be attributed to the oxygen vacancy redistribution. The excellent agreement of the stretched exponential fit (SEF) with the experimentally recorded decays additionally supports the previous assumption. For a positive applied bias, the curve shows an additional exponential growth in the beginning, followed by a retention loss according to Kohlrausch’s law, apparent in Figure 2d,e. Figure 2e shows the 10 postsynaptic currents for positive applied stimulation pulses at a frequency of 0.25 Hz. The curves are fitted with a SEF and an additional exponential growth term. The fitting equation is then given by

$$I(t) = -I_0 \exp(-\frac{t}{\lambda}) + I_{0,K} \exp\left(-\frac{t}{\tau}\right)^\beta$$

(2)

where $I_0$ is the amplitude of the growth and $\lambda$ is the growth time. The fits match very well to the curve shown in Figure 2e, where it becomes obvious that the growth time is increasing with pulse number and becomes even larger than the pulse interval, so that the decay is not seen anymore. This can also be seen in the fitting parameters, shown in Figure 3b,c. It is
observed, that the decay lifetime, as well as the growth time for positive biases, increase for increasing pulse numbers and frequencies (the fits for the negative applied bias are shown in Figure S2, Supporting Information). The stretching parameter $\beta$ is 0.5 for a negative applied bias and $\approx 0.2$ for a positive applied bias, resulting in a Kohlrausch decay. For a positive bias, large pulse numbers and high frequencies lead to a vanishing of the decay within the pulse interval, so that the lifetime value becomes insignificant. Especially at a frequency of 0.5 Hz the growth time outlasts the pulse interval completely.

The lifetime values range from milliseconds to seconds for a negative voltage and up to 100 s for a positive voltage and increase per pulse number similar to biological synapses. The increase of the SEF lifetime, which is observed for both polarities, is explained by an increased amount of accumulated oxygen vacancies at the top or bottom interface for large enough frequencies. A maximum lifetime for the present memristive devices has been observed previously to be around 20 min, which is due to a saturation of accumulated oxygen vacancies.[31] However, we observe lifetimes of smaller than 100 s for the SRDP measurements, which is in a similar range to the STP observed in human brains.[45] Furthermore, an exponential growth of the current has been seen in previous studies on nano batteries.[46] It has been related to a contamination of adsorbed species at the interface to the electrode. Indeed, the exponential growth is only observed, when oxygen vacancies accumulated at the bottom FTO interface (at positive bias). It is therefore suggested, that reactions of the oxygen ions from

Figure 2. a,b) SRDP for pulse voltages of $-2$ and 3.3 V for different frequencies. c,d) EPSC decays measured at 0.25 Hz for both polarities. e) Evolution of the transient current after stimuli. The growth of the current becomes more dominant with increasing pulse number until no decay is visible anymore within the pulse interval.

Figure 3. a) Schematic of the measurement protocol, where $f$ is the frequency. b) Fitting parameters for voltage stimuli of $-2$ V amplitude and c) for a stimuli amplitude of 3.3 V.
the FTO and the accumulated oxygen vacancies in the TiO$_x$ are taking place. It is likely, that oxygen vacancies migrate into the FTO upon applying the electric field. Upon removal of the field, the oxygen vacancies redistribute throughout the nanowire, increasing its conductivity. As this effect is even more pronounced for higher frequencies (Figure 2e and Figure 3c), it is concluded that the oxidation at the bottom nanowire could not relax back to equilibrium before the next voltage pulse, so that the growth time increases with each pulse number. It has to be mentioned, that it was not possible to fit the EPSC signals for a frequency of 0.67 Hz since the source meter did not record enough data to fit the curve properly.

Another way to compare the SRDP of TiO$_x$ nanowire emulators to biological synapses is to calculate the PTP and the PPF of the SRDP measurements. Therefore, the maximum current height difference between the first and tenth (PTP), as well as the first and second pulse (PPF), is calculated and shown in Figure 4. The lines are added only as a guide to the eye. For increasing intervals (smaller frequencies), the difference of the currents is small. However, for high enough frequencies, the transient current decay overlaps with the following stimulus, increasing the conductivity of the memristor. This means, that the redistribution of the oxygen vacancies competes with the following stimulation pulse, similar to the biological analog, where the action potential induces an influx of calcium ions into the presynaptic end. This leads to a release of neurotransmitters, inducing a synaptic potential at the postsynaptic region. If the next action potential reaches the presynaptic end before the synapse relaxed back to equilibrium, the resulting postsynaptic response is larger than the one before.$^{[17,47]}$ The strong dependence of the postsynaptic response to the action potential is schematically shown in Figure 5a. The respective dependence of the lifetime of the postsynaptic current of the TiO$_x$ memristors on the pulse amplitude is presented in Figure S5b,c. The respective SRDP measurements can be found in Figure S3, Supporting Information. A threshold voltage is observed for both polarities, where at a frequency of 0.5 Hz switching starts at $-1.5$ V for negative bias and at $2/3$ V for positive applied bias. This leads to even more bio realistic memristive devices, since a large enough action potential is necessary to transfer signals from one cell to another.$^{[7]}$ Furthermore, the lifetime, as well as the growth time, increase with larger amplitudes. This is due to a stronger field, making the oxygen vacancies more mobile and increasing the number of accumulated oxygen vacancies. Again, a larger amount of oxygen vacancies accumulates at the interfaces, needing more time to redistribute and hence, leading to a longer lifetime of the postsynaptic signal. The $\beta$ fitting parameter is again $\sim$0.5 for negative applied biases and $\sim$0.2 for positive applied bias, both lying in the region for stretched exponential functions ($0 < \beta < 1$).$^{[48]}$

Furthermore, 150 identical voltage pulses (3.3 and $-2$ V) with a frequency of 0.5 Hz are applied to the memristor. The transient current between pulses and after the pulse train is measured at 0.1 V and results are shown in Figure 6. The current increases with increasing pulse number until a steady state is reached. The transient current is probed afterward at 0.1 V, leading to a retention time of 100 s for the negative applied potential and a lifetime above 300 s for the positive applied potential, indicating the transition to a long term memory, as has been investigated before.$^{[31,48]}$ Altogether, this shows the possibility to emulate important functionalities of biological synapses by using TiO$_2$ nanorod arrays. However, for device application as artificial synapse in physical neuronal networks, the device architecture, and the structure’s dimensions need to be adjusted. Previous work already shows the possibility of position controlled growth and the impact of the growth parameters on the resulting structure of the nanowire$^{[49,50]}$ which can be used in further device engineering work on building physical neuronal networks based on TiO$_2$ nanowires.

3. Conclusion

The hydrothermally grown nanowires show great potential in emulating biological synapses. Human brain functionalities like learning and forgetting, especially a transition between short- and long-term memory, are possible to adapt with the present memristor. The switching mechanism could be related to an oxygen vacancy migration, with the redistribution perfectly following Kohlrausch’s law. However, for positive applied biases, an exponential increase before the transient current decay is observed, which is suggested to result from an interaction of the oxygen vacancies with the oxygen inside the FTO. The transition from a short- to long-term memory is therefore accompanied by an exponential increase of the postsynaptic

![Figure 4. Current difference between first and second, and first and tenth pulse, indicating PPF and PTP, respectively, for the two polarities.](image-url)
current for positive polarities. Negative applied potentials therefore seem more suitable for synaptic function emulation.

4. Experimental Section
The nanowires were directly grown on DI/Aceton/IPA cleaned FTO substrates. The substrates were placed inside a Teflon beaker containing 4 mL of hydrochloric acid (37%), 8 mL of DI water, and 350 µL of Titanium(IV) butoxide. The butoxide was added to the solution dropwise, while stirring the acid/water solution to prevent agglutination. The sealed beaker was placed in an oven at 220 °C for 2 h. Details on the growth mechanism of this method are given by Kalb et al.[5] The devices were investigated electronically with a home-built setup, using FTO as bottom contact and a gold tip (diameter ≈ 1 mm) as top contact. A Keithely 2400 was used to perform current-voltage measurements. The Keithley itself was controlled by a Matlab program.

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.

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Figure 5. a) Schematic of the action potential amplitude dependence of the synaptic potential amplitude and lifetime shown for a biological synapsis. b,c) Fitting parameter of the postsynaptic current for stimuli potentials of b) −2 and c) 3.3 V.

Figure 6. PPF of 150 identical voltage pulses for −2 and 3.3 V amplitude, with a probe voltage of 0.1 V on a logarithmic scale, whereas the inset shows the measurement procedure.
