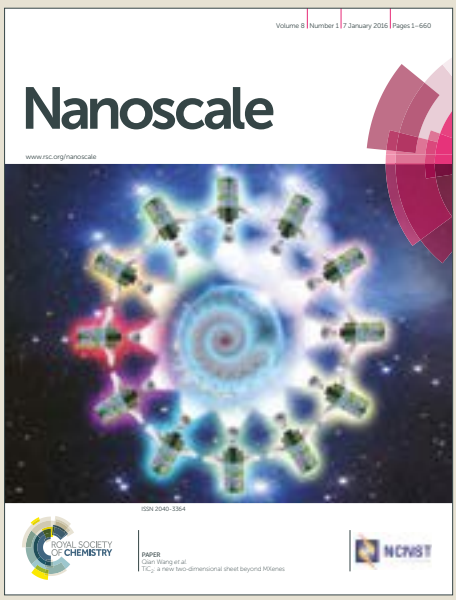
Nanoscale

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Hamdiyah, R. J. Gray, E. Verrelli, M. O'Neill, S. M. Kelly and N. T. Kemp, *Nanoscale*, 2017, DOI: 10.1039/C7NR06138B.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/nanoscale

Reversible Optical Switching Memristors with Tunable STDP Synaptic Plasticity: A Route to Hierarchical Control in Artificial Intelligent Systems

Ayoub Hamdiyah,[a] Robert J. Gray,[a] Emanuele Verrelli,[a] Mary O'Neill,[a] Stephen. M. Kelly[a] and Neil T. Kemp[a,*]

[a] School of Mathematics and Physical Sciences, University of Hull, Cottingham Rd, HU6 7RX, Hull, United Kingdom

* Author to whom correspondence should be addressed. Electronic mail: N.Kemp@hull.ac.uk

Keywords: memristor, optical, ZnO nanorod, azobenzene, resistive memory, synaptic plasticity

Abstract

Optical control of memristors opens the route to new applications in optoelectronic switching and neuromorphic computing. Motivated by the need for reversible and latched optical switching we report on the development of a memristor with electronic properties tunable and switchable by wavelength and polarization specific light. The device consists of an optically active azobenzene polymer, poly(disperse red 1 acrylate), overlaying a forest of vertically aligned ZnO nanorods. Illumination induces *trans-cis* isomerization of the azobenzene molecules, which expands or contracts the polymer layer and alters the resistance of the off/on states, their ratio and retention time. The reversible optical effect enables dynamic control of a memristors learning properties including control of synaptic potentiation and depression, optical switching between short-term and long-term memory and optical modulation of the synaptic efficacy via spike timing dependent plasticity. The work opens the route to the dynamic patterning of memristor networks both spatially and temporally by light, thus allowing the development of new optically reconfigurable neural networks and adaptive electronic circuits.

Introduction

View Article Online
DOI: 10.1039/C7NR06138B

Memristors are one of the most promising emerging technologies for the next generation of computer memory as they operate at high speed, have non-volatile low power operation and offer high-density integration.[1,2] Exhibiting electronic properties similar to synapses, memristors also emulate classic habituation learning phenomena[3] as well as spike timing dependent plasticity (STDP),[4] and are thus expected to transform neuromorphic computing[5] through the development of high density and low power neural networks for brain-inspired artificial intelligent systems. The reading and writing of memristors by light is particularly advantageous since light enables higher bandwidth signaling, faster transmission speeds, lower crosstalk and the ability to decouple circuits from unwanted electronic noise. Optical memristors should find use as new types of optical switches and memory elements in photonic integrated circuits and optical fiber telecommunications as well as applications in neuromorphic computing such as dynamically reconfigurable neural networks.

In this work, we report on the development of an optical memristor device with reversible latched switching that is controllable by the polarization of light. Few optical memristor devices have been reported. Devices have been demonstrated in which the electronic state of the memristor can be read by optical means.[6,7] However, a fully reversible latched optical switch exhibiting both an optical Set and optical Reset has not been reported.[8,9,10] In this work we report on such a device and use this to demonstrate a memristor with learning properties tunable by light. We show optical control of the synaptic potentiation and depression, optical switching between short and long term memory and optical modulation of the synaptic efficacy via spike timing dependent plasticity, which to the best of our knowledge has also not be been demonstrated in an optical memristor before. We envisage entirely new functionalities from the proof-of-principal concept demonstrated, including new dynamically reconfigurable memory elements and neural networks, tunable by light, and the potential to set the state (or synaptic plasticity) of individual elements in neural arrays during fabrication, thus saving valuable time and expense in training circuits post-production. In the latter case, the ability to pattern via light, regions or subgroups of memristors in a very large-scale neural network could enable hierarchical control of artificial intelligent systems, enabling, for instance, different learning behavior

in selected parts of an artificial brain. For instance, this could be used to implement learning properties specific to a particular sensory input (e.g. vision or auditory recognition) or used to pattern specific areas of memory with short-term or long-term memory.

Results and Discussion

Figure 1 schematically describes the unique hybrid organic-inorganic memristor device based on vertically aligned ZnO nanorods embedded within a photoactive azobenzene polymer poly(disperse red 1 acrylate), referred to as PDR1A. Irradiation of the device with wavelength- and polarization-specific light produces expansion (circularly polarized) or contraction (linearly polarized) of the PDR1A material enabling tuning of the electronic properties of the device.

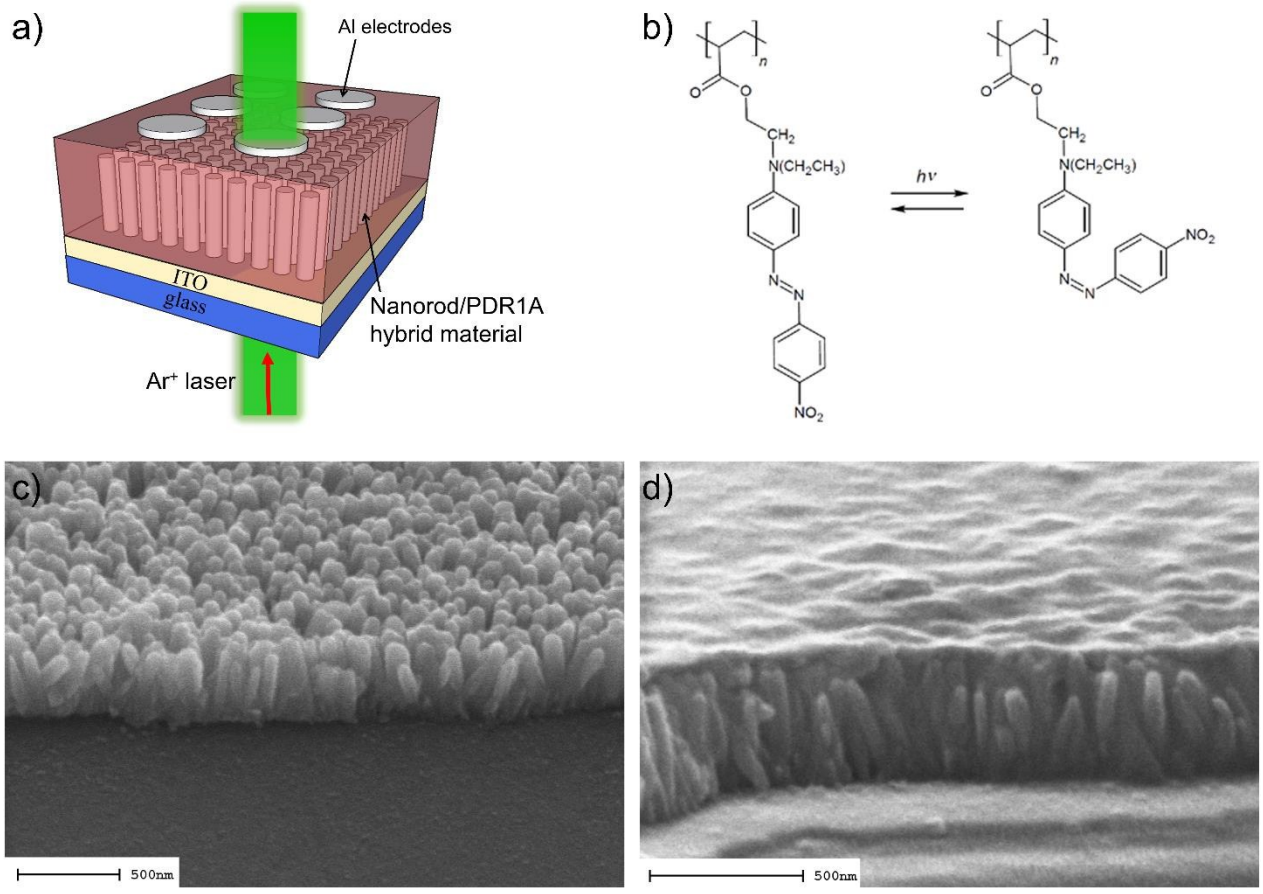


Figure 1. (a) Schematic of the optical memristor device consisting of **(b)** PDR1A molecules deposited onto **(c)** a thin-film of vertically aligned ZnO nanorods. The PDR1A material is deposited from solution as **(d)** a thin layer and partially diffuses into the voids between the ZnO nanorods.

View Article Online
DOI: 10.1039/C7NR06138B

Figure 2a shows the effect on film thickness of the PDR1A material when irradiated with light at 514 nm. Circularly polarized light increased the thickness from 113 nm to 147 nm, (~30%) whilst linearly polarized light reduced the thickness of the polymer back to its original state. This change is consistent with previous reports on azobenzene-containing polymers, e.g. a 17% increase was observed in a PDR1A sample with exposure to 488 nm light.[11] The expansion is attributed to an accumulation of the PDR1A chromophores with an out-of-plane alignment. Upon irradiation with wavelength and polarization specific light PDR1A undergoes a *trans-cis* photochemical isomerization upon optical excitation,[12,13] followed by a *cis-trans* thermal isomerization back to its original state (Figure 1b). Due to the overlap of the two absorption bands for the *trans-cis* and *cis-trans* transitions, *trans-cis-trans* cycling occurs, which is expected to play a central role in the process of aligning chromophores in the material upon irradiation with either circularly and linearly polarized light, which in turn leads to the expansion and contraction of the material, respectively.[14] Circularly polarized light prevents the orientation of the chromophores perpendicular to the direction of the beam (since all orientated azobenzene groups are activated) but tends to align the chromophores in the direction of the beam (since they become inert to the light). In the case of linearly polarized light, the chromophores tend to align in the direction perpendicular to the polarization of the beam as only those molecules that have a dipolar component along the laser polarization will be photoisomerized. In the former case, as the laser beam is perpendicular to the thin-film, the chromophores tend to become oriented in the out-of-plane direction, causing an expansion of the thin-film, whilst in the latter case, the orientation of the chromophore in-plane causes a reduction in film thickness.

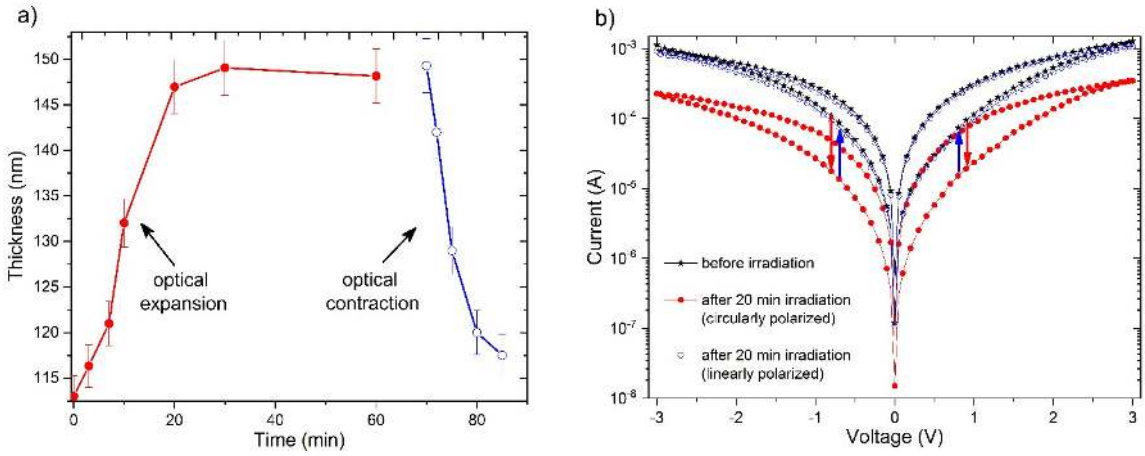
The effect of optical irradiation on the electronic properties of an ITO / ZnO / PDR1A / Al memristor device was investigated by performing I-V sweeps before and after optical irradiation. Figure 2b shows that after 20 min laser irradiation by circularly polarized light the I-V (red) curve has shifted to lower current. Associated with this is also a change in the resistance off/on ratio, from approximately 4 to 7, as determined by calculating the inverse gradient at a point close to the origin. Subsequent irradiation

View Article Online
DOI: 10.1039/C7NR06138B

with linearly polarized light demonstrates the effect is reversible, as shown by the shift in the I-V (blue) curve back to its original starting position.

The graph indicates the expansion or contraction of the polymer by irradiation with light shifts the entire hysteresis loop to either lower or higher current, respectively, without significant changes in either shape of the curve or the threshold switching voltage. This suggests that the expansion/contraction process affects only the conduction between the ZnO nanorods and the top metal electrode, and that the change in path length is the predominant reason why the conductance shifts to higher or lower values.

The mechanism of charge transport and switching in the devices was also examined. Fits of the current-voltage data to various charge transport models were employed and it was found that the most appropriate model was that of space charge limited conduction (SCLC) in the presence of traps, as shown and discussed further in Figure S2 of the Electronic Supplementary Information.



View Article Online
DOI: 10.1039/C7NR06138B

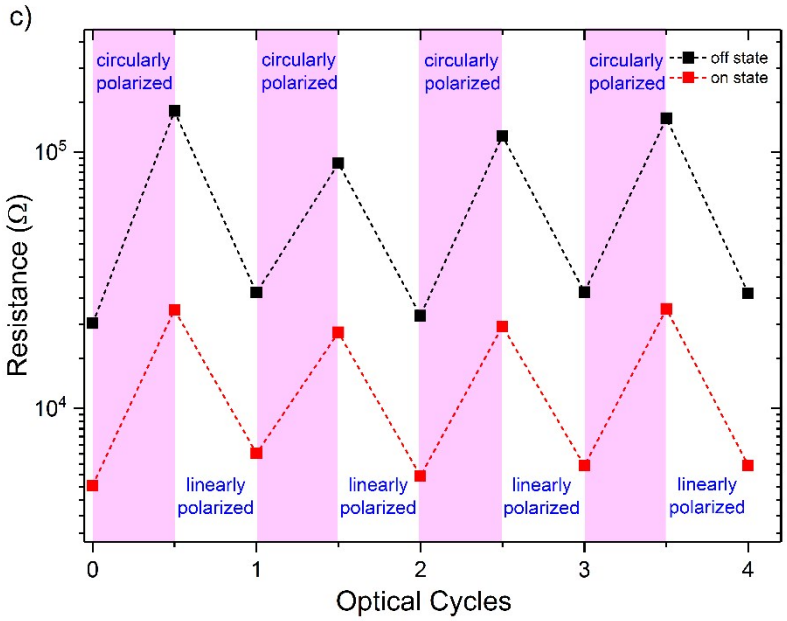


Figure 2 a) Expansion (●) and contraction (○) of the PDR1A film due to irradiation with circularly and linearly polarized light respectively. **b)** Optical modulation of the electronic switching characteristics of a ZnO/PDR1A memristor before irradiation (★), directly after irradiation (20 min) with circularly polarized light (●) and linearly polarized light (○). **c)** Optical modulation of the HRS and LRS states via repeated irradiation of circularly and linearly polarized light

Optical cycling of the memristor high resistance state (HRS) and low resistance state (LRS) was investigated by repeated irradiation of the device with 20 minute cycles of circularly and linearly polarized light. Figure 2c shows a plot of the device resistance of the HRS (black curve) and LRS (red curve) states as a function of time. The graph indicates the periodicity of the switching matches that of the cycling of the circularly polarized and linearly polarized irradiation (pink and white colored vertical bars).

In the following, we investigate the potential of the device in controlling the neuromorphic learning properties of memristors by optical means. Hebbian theory[15] postulates that synapses in the brain "learn" by adapting to repeated signaling events. Synaptic plasticity is a measure of this response

View Article Online
DOI: 10.1039/C7NR06138B

over time and involves either a weakening or strengthening of the synaptic connection. In the case of a memristor, the synaptic strength is akin to a measurement of its electrical resistance. In Figure 3a, the effect of pulsed optical irradiation on the synaptic plasticity of the device is shown. The graph indicates that repeated exposure to pulses of circularly polarized light followed by pulses of linearly polarized light causes first depression, as shown by an decrease in the conductance, and then potentiation, as indicated by an increase in conductance, proving that optical stimulus can modulate the synaptic plasticity of the memristor device. Figure 3b demonstrates a similar effect is also achieved by purely electrical stimulus, in this case via the application of voltage pulses of 2.0 V with pulse length of 50 ms.

Spike-timing-dependent plasticity (STDP) is also a key tenet of Hebbian learning and has been shown to be linked with sensory perception, spatial reasoning, language and conscious thought in the neocortex.[16] In STDP, learning and information storage is dependent upon the difference in arrival times of action potentials from neighboring neurons, called pre-synaptic and post-synaptic spikes, as shown in Figure 4b and 4c. The arrival of overlapping pulses can strengthen (potentiation) or weaken (depression) the synaptic efficacy. In memristors, synaptic efficacy can be quantified by the change in conductivity of the device.[17] Figure 4a demonstrates the effective modulation of the memristor synaptic efficacy (△G/G) by light as shown by measuring the synaptic efficacy before and after illumination by circularly polarized light. The effect is reversible via irradiation with linearly polarized light and can be modulated by varying the irradiation time or laser intensity. The lines are fits to the asymmetric Hebbian STDP learning rule[18–20]

$$\Delta w = \begin{cases} A_+ e^{-|\Delta t|/\tau_+} & if\ \Delta t > 0 \\ A_- e^{-|\Delta t|/\tau_-} & if\ \Delta t < 0 \end{cases} \quad (1)$$

where Δw is the change in the synaptic efficacy, Δt is the time difference between the pre and post spikes, and $A_{\pm}$, $\tau_{\pm}$ are parameters representing the amplitude and time constants, respectively.

View Article Online
DOI: 10.1039/C7NR06138B

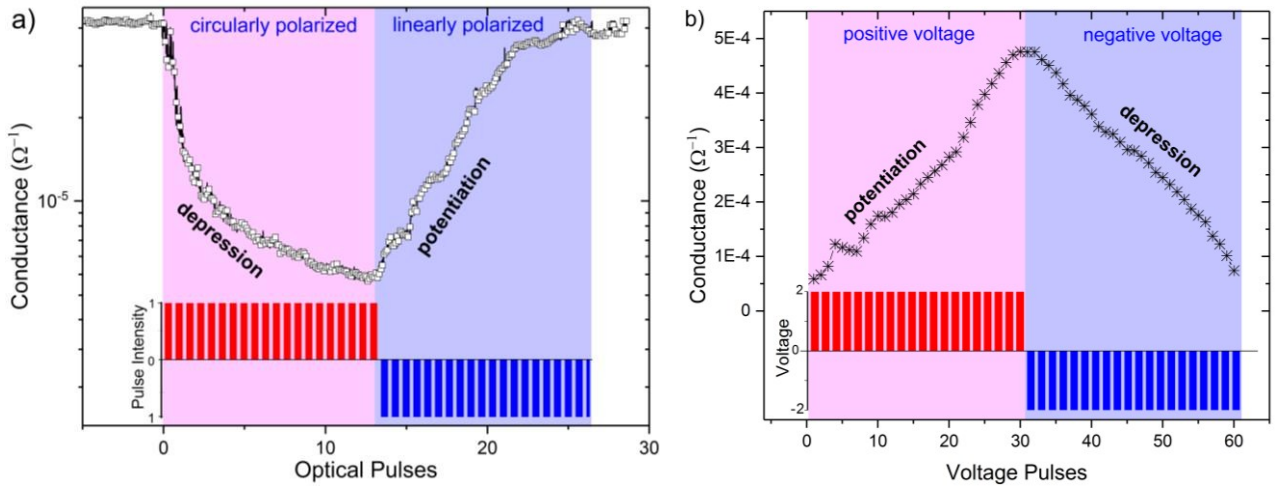


Fig. 3 a) Classical habituation phenomenon controlled by purely optical means as demonstrated by the incremental decrease (depression) and increase (potentiation) of the conductance of the LRS state with repeated pulses of circularly polarized (red) and linearly polarized (blue) light. **b)** Habituation controlled by purely electrical means through the application of positive and negative voltage pulses resulting in increasing and decreasing conductance respectively.

The sequence of pulses used to obtain the synaptic efficacy curve were the following: 1. an initialization pulse of -2.0 V (length 100 ms) was used to reset the device to an initial off state. 2. a read (probe) pulse of 0.15 V (150 ms) was used to determine the conductance state of the device, 3. the synaptic efficacy of the device was modified by applying a single paired spike sequence consisting of two pulses (pre-spike and post-spike) of the form shown in Fig 4b and separated by different times ranging from -1.0 to +1.0 s, 4. a final read (probe) pulse of 0.15 V (150 ms) was used to determine the final conductance state of the device. The conductance (probe) measurements taken in Figure 4a) were carried out using a HP4140B picoammeter in combination with a Keithley 230 V voltage source, whilst the voltage and current traces in Figure 4c) and 4d) were obtained using a different setup consisting of a Keithley 230 V and a two-channel Keysight InfiiVision oscilloscope

View Article Online
DOI: 10.1039/C7NR06138B

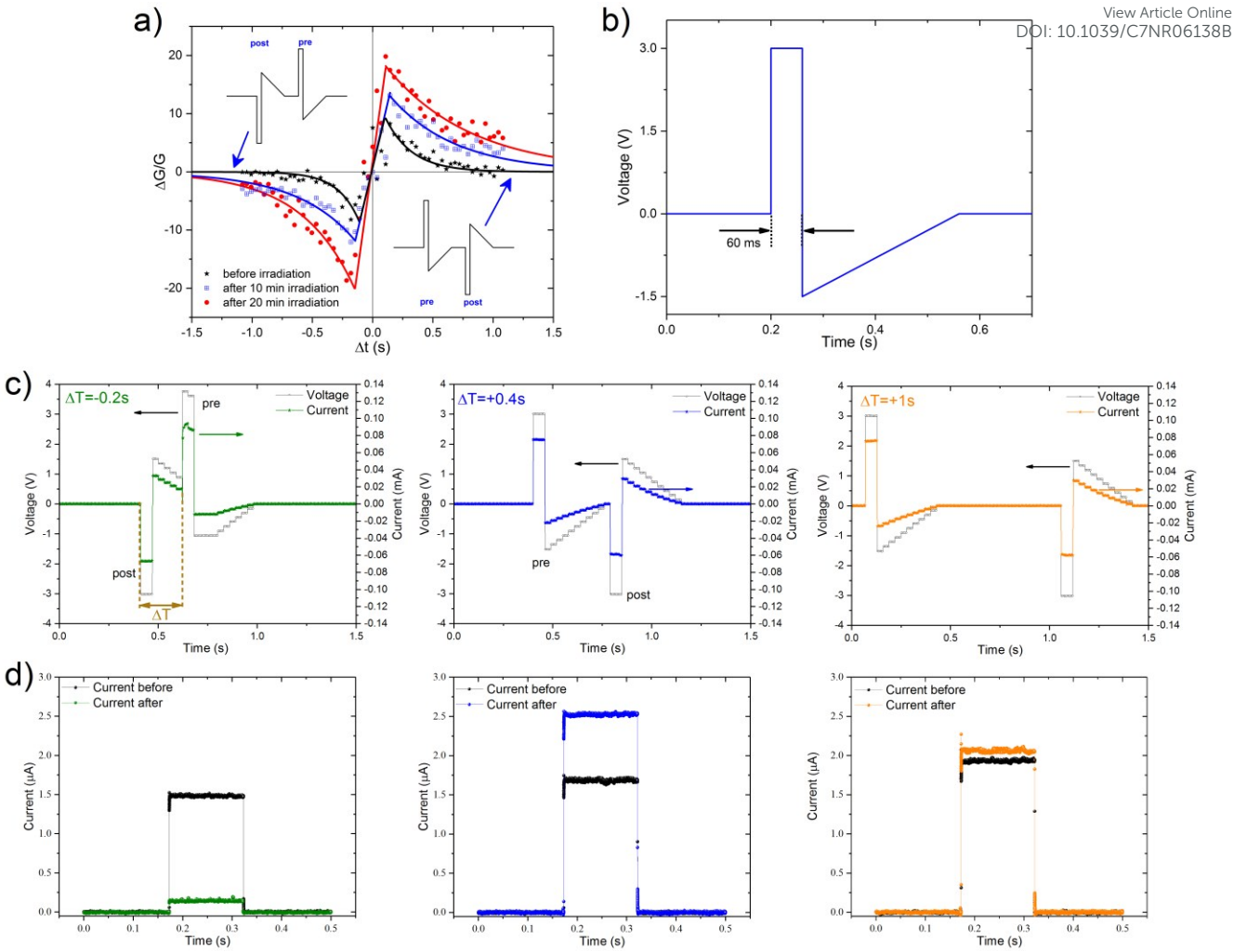


Figure 4. a) Optical modulation of the STDP synaptic efficacy, showing optically tunable learning, as demonstrated by a shift in the synaptic efficacy curves before and after optical irradiation. The synaptic efficacy curves are obtained by measuring the change in conductance (△G/G) vs. different arrival times (△t) of the pre and post synaptic pulses. The lines are fits to the asymmetric Hebbian STDP learning rule. **b)** Shape of the voltage pulse used to simulate the action potentials. **c**) Representative current traces from a device during STDP implementation with different pre and post synaptic pulse separation times of ΔT = -0.2, 0.4 and 1 s. **d**) Measurement of the current through the device, using a small voltage pulse, before and after each of the corresponding paired STDP measurements in c).

View Article Online
DOI: 10.1039/C7NR06138B

Lastly, we show how the optical memristor device can be used to control the lifetime of memory states, allowing short-term, medium-term and long-term (non-volatile) memory storage. In Figure 5 the retention time of the memristor device was measured in two different scenarios. The medium-term memory state is achieved by firstly irradiating the device with circularly polarized light for twenty minutes. This process acts as a switch and turns the optical memory device to the "on" state, i.e. information is written to device. The information is erased by turning off the light source. This permits a slow thermal relaxation process to occur, which contracts the PDR1A thin-film and resets the device to its initial state. The switch to the "off" state occurs with a characteristic time constant, τ_m. Contraction via thermal relaxation is a slow process and typically occurs 8 times slower than when devices are irradiated with linearly polarized light (see Figure S1 in Electronic Supplementary Information). In the short-term memory scenario, information is written in the same manner i.e. the device is switched to the "on" state using circularly polarized light. To erase this information, i.e. to switch the device to the "off" state, the device is exposed to linearly polarized light, which contracts the polymer at a much faster rate than the medium term "thermal relaxation" process. In this case the characteristic time constant, τ_s, is much shorter i.e. $\tau_s < \tau_m$. Overall, the short-term and medium-term memory processes are similar to STP and LTP processes in biological systems, which involve enhancement of the connection strength between two neurons but with different decay rates back towards their initial states. However, since we have defined the synaptic efficacy in terms of conductance (resistance could instead be used), a more precise definition, in our case would be that the devices exhibits short-term depression (STD) and long-term depression (LTD) since the optical irradiation by circularly polarized light diminishes the conductivity of the device. In the case of the medium-term memory effect observed in this article, the switch back to its initial states is a spontaneous event and is therefore consistent with LTD, but in the case of the short-term memory effect, the process is a little different as it is an activity dependent process involving optical stimulation.

Optically controllable short-term and long-term memory and dynamic modification of the retention time of stored information could have application in freeing up information that is stored for different

View Article Online
DOI: 10.1039/C7NR06138B

purposes. For example, the medium term memory approach would enable data to be stored for a reasonable amount of time before being automatically forgotten. This would save the system energy and time in having to perform a specific erase process. In an artificial intelligent system an application of this could include memory needed for episodic memory or used to give spatial awareness. In the short memory scenario, optical irradiation could be used to erase data that is not needed for a long period of time, applications could include memory used in numerical calculations, logic operations or cache memory. In the latter case improved switching times are likely needed, but perhaps not significantly so, since short-term memory in biological systems is approximately only 10-20 seconds and signaling processes themselves are typically only of the order of millisecond. The devices also exhibit long-term (non-volatile) memory (not shown). This involves operation of the memristor device by purely electrical signals (i.e. without any optical stimulus), whereby HRS and LRS state are achieved by the standard approach of electrical pulses.

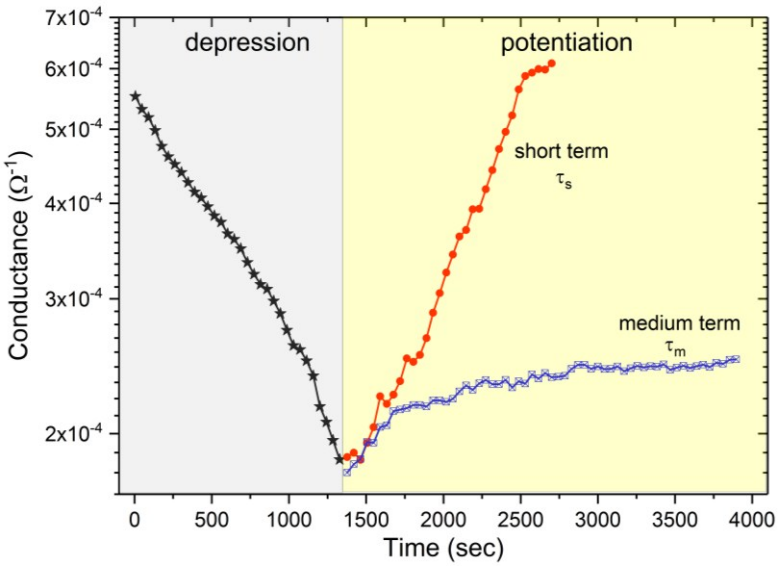


Figure 5. Optical modulation of memory retention to give short term and medium term memory as shown by the increase of the conductance with two different time constants following an initial irradiation by circularly polarized light (★). The medium term memory process (☒) does not involve optical irradiation but occurs due to thermal relaxation of the polymer whilst the short-term memory process (●) involves irradiation with linearly polarized light, which contracts the polymer more quickly.

View Article Online
DOI: 10.1039/C7NR06138B

Overall, we have shown that irradiation by wavelength- and polarization-specific light can be used to modulate the resistance of memristor states (Figure 2). The effect is reversible and repeatable with time, as demonstrated through multiple cycles of irradiation by circularly and linearly polarized light. In the following, we discuss how this could be used to control the learning properties of a memristor and its importance in developing more complex artificial brain-like systems through hierarchical control.

In biological synapses the connection strength (plasticity) between two neurons is controlled by the ionic flow through the synaptic cleft and it is widely believed that the adaptation of synaptic weights enables biological systems to learn and function. Similarly, the conductance of a memristor depends on the history of the total charge that has travelled through it. A key feature of neuronal learning is habituation, whereby repeated stimuli strengthens the synaptic plasticity whilst a lack of stimuli results in weakening. Memristors too exhibit this phenomenon and therefore emulate the learning properties of synapses in the brain.[3] In memristors, this is typically achieved via electronic means, as shown in Figure 3b, through the application of repeated voltage pulses. In contrast, in Figure 3a we demonstrate an optical analogue, whereby habituation is instead controlled by purely optical means. This was achieved through the application of optical pulses of circularly and linearly polarized light, which produced changes in the resistance of the memristor that are consistent depression and potentiation curves, respectively, observed in biological synapses.

Learning in biological systems also involves spike-timing-dependent plasticity (STDP). In STDP learning the synaptic efficacy governing potentiation and depression is determined instead by the temporal order of pre-synaptic and post-synaptic spikes. In Figure 4a we demonstrate that optical irradiation of our memristor device can also be used to control the synaptic efficacy. Time differentiated electronic STDP voltage pulses, of the spike-shape waveform approximately expected in biological neurons (see Figure 4b), were supplied to the memristor to mimic action potentials

View Article Online
DOI: 10.1039/C7NR06138B

generated from two attached neurons. The synaptic efficacy, measured as the change in conductance (△G/G) of the memristor, is plotted before and after irradiation by circularly polarized light. The results show that much larger STDP potentiation and depression are observed after optical excitation of the memristor. The effect demonstrates that optical control could be used as a means to control the characteristics of learning in memristor neural circuits.

In this work we have focused on the control of a single memristor device. The development of a system fully capable of emulating the brain's complex functions would require the orchestration of a complex network of billions of memristors divided into regions each having different functionality and learning characteristics. The dual control of a memristor both optically and electronically would support this ability to develop greater complexity. For example, light can provide hierarchical control, facilitating such processes as memory consolidation, synaptic pruning and conversion of short term to long-term memory. Light too can be used to function in a similar manner to hormones in the human body, offering localized and specific control. For example the stress hormone, corticosterone, modulates only the LTP/LTD plasticity of hippocampal synapses,[21] whereas metabolic hormones control synaptic plasticity in the hypothalamus to regulate hunger.[22] Optical control of synaptic plasticity could also have importance in the learning of new memories. In the mammalian hippocampus, a region important for spatial and episodic memory, newly generated neurons have specific mechanisms that control the synaptic plasticity more effectively,[23] thereby allowing neuronal pathways in this region to be more adept at learning new memories, such as those needed to give spatial awareness or information typically encountered on a daily basis. Since a memristor-based "brain" would only have a finite number of memristors, a process such as this would be needed to refresh synaptic pathways. In this manner, light could be used to erase synaptic pathways or regions of memory that are no longer required, changing their synaptic plasticity so they are more sensitized to learning new information.

Conclusions

View Article Online
DOI: 10.1039/C7NR06138B

In summary, we have demonstrated a memristor device that exhibits reversible and latched optical switching that is controllable by illumination with polarization specific light. This is achieved *via* a hybrid organic-inorganic materials approach in which optical functionality is introduced by incorporating an optically active polymer material with resistive switching ZnO nanorods. We show that modulation of the electrical properties of memristors by light provides a new level of functionality that supports the development of entirely new types of devices and circuits. In optoelectronics, applications include optical switches for integrated photonic circuits and adaptive electronics, whereas in neuromorphic computing applications, the spatial and temporal patterning of memristor arrays by light opens the route to dynamically tunable and reprogrammable synaptic circuits as well as hierarchical control in artificial intelligent systems. In this article we show how the devices can be used to implement optically tunable Hebbian learning and STDP synaptic plasticity, which permits a route to hierarchical control in artificial intelligent systems. In the future, we envisage the use of polymers with faster expansion/contraction speeds will be of benefit for optoelectronic and neuromorphic applications whilst the incorporation of UV cross-linkable polymers could enable the development of mass produced neural circuits in which light sets the synaptic plasticity or state of the memory element, eliminating the need of training post-production.

Methods

The devices consist of a vertical thin-film sandwich structure (Figure 1a) with the following sequence of materials, ITO / ZnO nanorods / PDR1A / aluminum. Vertically aligned ZnO nanorods were grown onto indium tin oxide (ITO) coated glass using an ultrafast microwave growth technique similar to that previously reported.[24,25] The first step consists of seeding ZnO nucleation sites by spin-coating three successive times (2000 rpm for 30s) a 10 mM solution of zinc acetate dehydrate (98%, Sigma Aldrich). Alignment of the nanorods was achieved by annealing the seed layer at 350°C for 30 minutes.[26] Nanorod growth consisted of suspending the substrates upside down in a closed reaction tube

View Article Online
DOI: 10.1039/C7NR06138B

containing an equimolar mixture of 25 mM zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) and hexamethylenetetramine (Sigma Aldrich) in deionized (DI) water and heating in a microwave oven at 100 W for 30 minutes at a maximum temperature of 80ºC. Afterwards the devices were cleaned by rinsing in DI water with drying under nitrogen flow. Figure 1 (c) shows a SEM image of a typical ZnO nanorod thin-film with nanorods approximately 200 nm in length (note: nanorods appear to be longer due to the 70º sample tilt used in the SEM imaging) with diameters of 40-50 nm.

Poly(disperse red 1 acrylate), i.e., poly(4'-{[2-(acryloyloxy)ethyl]ethylamino}-4-nitroazobenzene), purchased from Sigma Aldrich, was dissolved in tetrahydrofuran (20 mg/ml) and spin coated at 1000 rpm for 30 s onto ZnO nanorod coated ITO substrates. The films were heated above the glass transition temperature of the polymer, ~95°C, to remove any remaining solvent. The PDR1A film thickness on glass substrates was typically 110 nm but for ZnO nanorod coated ITO substrates the film thickness is smaller as indicated by the SEM image in Figure 1d. This is likely due to differences in the wettability and frictional forces of the nanorod surface in contrast to glass. The undulating top surface of the PDR1A thin-film also indicates penetration of the PDR1A molecules into the voids between the nanorods, which makes it difficult to ascertain an accurate value for the film thickness. Top contacts, aluminum (200 nm thick), were deposited by thermal evaporation under vacuum conditions through a mask containing 400 µm diameter circles. I-V sweeps were carried out using a probe station equipped with an HP4140B source-meter unit. Photomechanical expansion/contraction was induced by irradiation with circular/linear polarized light from an Argon ion laser tuned to 514 nm. The spot size of the laser beam had a diameter of 3 mm and the average power per unit area for the exposed device was 180 mW/cm^2. Characterization of the effects of optical irradiation on just the PDR1A material was carried out using a profiling system (Bruker Dektak) on a series of PDR1A thin-films deposited onto glass.

Conflicts of interest

There are no conflicts of interest to declare.

View Article Online
DOI: 10.1039/C7NR06138B

Acknowledgments

We would like to sincerely thank support from the Iraqi Ministry of Higher Education and Scientific Research (University of Baghdad) for partial funding of this work and help with SEM imaging from Garry Robinson (School of Engineering, University of Hull). The authors would like to acknowledge the contribution of the COST Action IC1401.

References

(1) Kim, K.-H.; Gaba, S.; Wheeler, D.; Cruz-Albrecht, J. M.; Hussain, T.; Srinivasa, N.; Lu, W. A Functional Hybrid Memristor Crossbar-Array/CMOS System for Data Storage and Neuromorphic Applications. *Nano Lett.* **2011**, *12*, 389–395.

(2) Khiat, A.; Ayliff, P.; Prodromakis, T. High Density Crossbar Arrays with Sub- 15 Nm Single Cells via Liftoff Process Only. *Sci. Rep.* **2016**, 1–8.

(3) Chua, L. O. Memristor, Hodgkin-Huxley, and Edge of Chaos. *Nanotechnology* **2013**, *24*, 383001.

(4) Jo, S. H.; Chang, T.; Ebong, I.; Bhadviya, B. B.; Mazumder, P.; Lu, W. Nanoscale Memristor Device as Synapse in Neuromorphic Systems. *Nano Lett.* **2010**, *10*, 1297–1301.

(5) Indiveri, G.; Linares-Barranco, B.; Legenstein, R.; Deligeorgis, G.; Prodromakis, T. Integration of Nanoscale Memristor Synapses in Neuromorphic Computing Architectures. *Nanotechnology* **2013**, *24*, 384010.

(6) Emboras, A.; Goykhman, I.; Desiatov, B.; Mazurski, N.; Stern, L.; Shappir, J.; Levy, U. Nanoscale Plasmonic Memristor with Optical Readout Functionality. *Nano Lett.* **2013**, *13*, 6151–6155.

(7) Hoessbacher, C.; Fedoryshyn, Y.; Emboras, A.; Melikyan, A.; Kohl, M.; Hillerkuss, D.; Hafner, C.; Leuthold, J. The Plasmonic Memristor: A Latching Optical Switch. *Optica* **2014**, *1*, 198.

(8) Tan, H.; Liu, G.; Zhu, X.; Yang, H.; Chen, B.; Chen, X.; Shang, J.; Lu, W. D.; Wu, Y.; Li, R. W. An Optoelectronic Resistive Switching Memory with Integrated Demodulating and Arithmetic Functions. *Adv. Mater.* **2015**, *27*, 2797–2803.

(9) Wang, W.; Panin, G. N.; Fu, X.; Zhang, L.; Ilanchezhiyan, P.; Pelenovich, V. O.; Fu, D.; Kang, T. W. MoS2 Memristor with Photoresistive Switching. *Sci. Rep.* **2016**, *6*, 31224.

(10) Huebner, C. F.; Tsyalkovsky, V.; Bandera, Y.; Burdette, M. K.; Shetzline, J. A.; Tonkin, C.; Creager, S. E.; Foulger, S. H. Nonvolatile Optically-Erased Colloidal Memristors. *Nanoscale* **2015**, *7*, 1270–1279.

(11) Yager, K. G.; Tanchak, O. M.; Godbout, C.; Fritzsche, H.; Barrett, C. J. Photomechanical Effects in Azo-Polymers Studied by Neutron Reflectometry. *Macromolecules* **2006**, *39*, 9311–9319.

(12) Rau, H. *In Photochemistry and Photophysics*; J. K. Rabek, Ed.; CRC Press: Boca Raton, FL,

View Article Online
DOI: 10.1039/C7NR06138B

1990.

(13) Natansohn, A.; Rochon, P. Photoinduced Motions in Azo-Containing Polymers. *Chem. Rev.* **2002**, *102*, 4139–4175.

(14) Tanchak, O. M.; Barrett, C. J. Light-Induced Reversible Volume Changes in Thin Films of Azo Polymers: The Photomechanical Effect. *Macromolecules* **2005**, *38*, 10566–10570.

(15) Hebb, D. O. *The Organization of Behaviour*; Wiley: New York, 1949.

(16) Markram, H.; Lubke, J.; Frotscher, M.; Sakmann, B. Regulation of Synaptic Efficacy by Coincidence of Postsynaptic APs and EPSPs. *Science (80-.).* **1997**, *275*, 213–215.

(17) Serrano-Gotarredona, T.; Masquelier, T.; Prodromakis, T.; Indiveri, G.; Linares-Barranco, B. STDP and sTDP Variations with Memristors for Spiking Neuromorphic Learning Systems. *Front. Neurosci.* **2013**, *7*, 1–15.

(18) Bi, G. Q.; Poo, M. M. Synaptic Modifications in Cultured Hippocampal Neurons: Dependence on Spike Timing, Synaptic Strength, and Postsynaptic Cell Type. *J. Neurosci.* **1998**, *18*, 10464–10472.

(19) Gerstner, W.; Ritz, R.; van Hemmen, J. L. Why Spikes? Hebbian Learning and Retrieval of Time-Resolved Excitation Patterns. *Biol. Cybern.* **1993**, *69*, 503–515.

(20) Zhang, L. I.; Tao, H. W.; Holt, C. E.; Harris, W. a; Poo, M. A Critical Window for Cooperation and Competition among Developing Retinotectal Synapses. *Nature* **1998**, *395*, 37–44.

(21) Kim, J. J.; Diamond, D. M.; Haven, N.; Blvd, B. B. D. The Stressed Hippocampus, Synaptic Plasticity and Lost Memories. *Nat. Rev. Neurosci.* **2002**, *3*, 453–462.

(22) Yang, Y.; Atasoy, D.; Su, H. H.; Sternson, S. M. Hunger States Switch a Flip-Flop Memory Circuit via a Synaptic AMPK-Dependent Positive Feedback Loop. *Cell* **2011**, *146*, 992–1003.

(23) Schmidt-Hieber, C.; Jonas, P.; Bischofberger, J. Enhanced Synaptic Plasticity in Newly Generated Granule Cells of the Adult Hippocampus. *Nature* **2004**, *429*, 184–187.

(24) Verrelli, E.; Gray, R. J.; O'Neill, M.; Kelly, S. M.; Kemp, N. T. Microwave Oven Fabricated Hybrid Memristor Devices for Non-Volatile Memory Storage. *Mater. Res. Express* **2014**, *1*, 46305.

(25) Unalan, H. E.; Hiralal, P.; Rupesinghe, N.; Dalal, S.; Milne, W. I.; Amaratunga, G. A. J. Rapid Synthesis of Aligned Zinc Oxide Nanowires. *Nanotechnology* **2008**, *19*, 255608.

(26) Greene, L. E.; Law, M.; Tan, D. H.; Montano, M.; Goldberger, J.; Somorjai, G.; Yang, P. General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds. *Nano Lett.* **2005**, *5*, 1231–1236.