Paper

Memristive perovskite solar cells towards parallel solar energy harvesting and processing-in-memory computing

Konstantinos Rogdakis,[a,b*] Michalis Loizos[a], George Viskadouros[a] and Emmanuel Kymakis [a,b*]

Received 8th April 2022,
Accepted 00th xxxx 2022

DOI: 10.xxxx/x0xx00000x

The peculiar ions and carriers heterogeneity observed in hybrid organic / inorganic materials is the source of their emergent cross-coupled light and electric field tuneable functions with potential utility in novel opto-electronic applications. Notably, mixed halide perovskites (HP) have been used as active layer in highly performing perovskite solar cells (PSC) that had led to efficient solar energy harvesting. Their rich dynamics enabled by the inherently coupled ionic and electronic degrees of freedom have also led to the demonstration of optoelectronic memristors that emulate synaptic- and neural- like dynamics. Consequently, a printable single material stack fabricated at low temperature, combining both solar energy harvesting and memristive functionalities attainable at low switching voltages would constitute a transformational breakthrough. In this study, we demonstrate an inverted PSC with an average power conversion efficiency (PCE) of ~17% that upon appropriate electric biasing procedure exhibits stable resistance switching characteristics at low voltages without losing its PCE performance even after thousands of switching cycles (hereafter this device is termed as MemPVCell). Specifically, the MemPVCell demonstrates a High Resistance State (HRS) to Low Resistance State (LRS) ratio of up to 10^5, light-tunable switching cycles in millisecond regime with endurance of $3x10^3$ cycles with no detectable HRS/LRS ratio drop. During state retention tests, HRS exhibits no change in time while LRS gradually increases resulting to an overall HRS/LRS ratio retention of up to 3600 s with less than 30% drop of its initial value in the optimum device configuration. Corresponding PCE performance was monitored after performing multiple dc resistance switching loops and pulsed endurance cycles, demonstrating a full PCE recovery to its initial value within few minutes of rest. Complementary transient electrochemical impedance spectroscopy (EIS) measurements supported the MemPVCell switching effects. Aiming at improving further the device performance, modifications of MemPVCell's layered structure were investigated, a process that allowed to identify each layer impact on the parallel photovoltaic and memristive switching characteristics. As a proof of concept towards light-controlled neuromorphic circuits, basic synaptic functionalities are demonstrated such as potentiation and depreciation protocols, short-term plasticity (STP) and long-term plasticity (LTP) effects as well as associated spike-timing dependent plasticity (STDP).

Introduction

Technologies implementing autonomous smart devices into an Internet-of-Things (IoT) network are increasingly required in our society. A largely distributed network of wireless sensors and wearables are currently connected in the cloud. One of the most challenging bottlenecks in achieving the future vision of IoT involves powering a multitude of devices, posing critical requirements therefore on their power consumption. These IoT platforms create a robust demand for energy for their power supply, while their ever-increasing number, requires ultra-low-power edge-device computing for big data processing.[1] The inherent bottlenecks of Si-based CMOS processors due to their energy inefficient von Neumann's computation architecture associated to the 'memory wall' issue,[2] lead to unsustainable energy cost in IoT data-centric intensive tasks.[3] IoT edge devices[4] are usually not capable of data processing and rely on energy-consuming and high-latency cloud communication. Most Si-based IoT devices depend on a battery as their power source, therefore, fail to meet the design goals of lifetime power supply, low-cost, reliable sensing, and secure data transmission, demanding radically new material approaches, as well as novel device physics and computing principles.

Energy harvesting is a potential alternative to evade recurrent battery replacement, while distinct neuromorphic memristive crossbar arrays are promising solutions for IoT-oriented energy efficient computing,[5] pattern recognition and visual pre-processing,[6] presenting unique advantages over von Neumann

[a] Department of Electrical & Computer Engineering, Hellenic Mediterranean University (HMU), Heraklion 71410 Crete, Greece.
[b] Institute of Emerging Technologies (i-EMERGE) of HMU Research Center, Heraklion 71410, Crete, Greece.
*e-mails: krogdakis@hmu.gr, kymakis@hmu.gr .

† Electronic supplementary information (ESI) available: Extra memristive switching and PV characteristics at various electrical and illumination conditions; Transient photovoltage (TPV) and photocurrent (TPC), photo-Celiv, External Quantum Efficiency (EQE) spectra, electrochemical impedance spectroscopy (EIS), data See DOI: …

architectures. Several emerging device concepts beyond von Neumann architecture has led to some successful commercial products, such as Adesto's Moneta electrochemical metallization memory for low-energy applications.[7] Two terminal (2T) memristors have attracted great interest as single synaptic units with high scalability, 3D integration capability, and fast switching speed.[3,5,6] Large area memristors crossbar arrays have the potential to perform vector-matrix multiplication directly utilizing Ohm's & Kirchhoff's law, while their inherent properties render them suitable for both digital and analogue computation.[3]

Memristors' processing-in-memory can impact numerous application areas upon resolving the sneak path current and half-select issues.[3,5] Conventional memristors operating in linear regime are outputting high currents, potentially limiting their power efficiency and scalability.[5–7] Alternatively, lower conductance nonlinear memristors, such ferroelectric based, have the potential for linear computation at ultralow currents towards 100 Gops/mW.[8] Optoelectronic memristors[9] have become promising candidates for artificial vision allowing temporary memory and real-time processing of visual information and sensory data.[6] However, challenges remain such as reliability, device-to-device variation, large-scale integration due to sophisticated fabrication and complex device architectures (rigid, costly), hindering memristive hardware from going mainstream.

The first generation of neuromorphic synaptic devices were based on oxide memristors and have demonstrated advantages in scalability, speed, and power consumption. However, "scaling up" toward a practical system size by "scaling down" device dimensions is increasingly challenging.[10] New approaches in materials, device, architecture, and algorithm design are necessary to emulate the scale, functional connectivity, and energy efficiency of the biological spiking neural networks.

Hybrid organic/inorganic material-based electronics offers the promise of a mixed ionic/electronic conductivity that has led to systems exhibiting basic functions of neural networks, including synaptic-level functions, such as short- and long-term plasticity (STP & LTP), and system-level properties such as spatiotemporal processing and homeostatic control.[11–14] The mechanical properties of organic materials match those of tissues, and the working mechanisms, involving ions, in addition to electrons, are compatible with human physiology.[15] Another advantage of organic materials is the potential to introduce novel fabrication techniques relying on additive manufacturing (AM) amenable to one-of-a-kind form factors, making printable organic neuromorphic devices a perfect fit where bioinspiration and bio-integration are required.[15]

Among the many other types of electronic devices[16–22], perovskite materials were also utilized in memristor devices, initially in their oxide form before the emergence of mixed halide perovskite (HP) materials, due to their ferroelectric properties.[23] HP owing to their intrinsic hysteresis and abundance of charge migration pathways are very promising for memristor applications,[24–29] apart from their exceptional power conversion efficiency (PCE) acting as active layers in solar cells.[30,31,32,33] Since the first report on organic-inorganic HP-based memristors[34], various perovskite compounds have been employed: These include HP[35], 2D organic-inorganic[36], all-inorganic perovskites[37], and lead-free[38] perovskites. Notably, hybrid HP also intrinsically incorporate richer dynamics in their switching behavior when compared to their inorganic counterparts. Specifically for HP, apart from the coexistence and coupling of ionic and electronic degrees of freedom, unique is also the light/electrically tunable majority carrier concentrations opening the path to solar brain realization.[1,39] Moreover, hybrid HP perovskites were used in memristive devices that can be programmed to two or more stable conductance states for analogue computing.[10]

Resistive switching in perovskites is reported to have an either electroforming origin attributed to the formation and rupture of a conductive filament between the bottom and top electrode[40,41] or an interface-dominated switching mechanism[42,43]. In **Table S1**, a literature summary of various perovskite-based memristors is shown in comparison with the devices of the present study indicating their high endurance. In the majority of the reported studies, the electrochemically active Ag is used as top electrode thus the application of electric bias results in Ag cations migration and the formation of a conducting bridge between the Ag top and the bottom electrode (usually ITO or Pt). The chemical composition of perovskite active layer was shown to affect the memristive properties of the devices, whereas the mobile Br^-, MA^+ and I^- are reported to be the sources of the limited endurance and retention characteristics.[27,41] Specifically, the incorporation of multiple cations such as Rb while suppressing MA/ Rb ratio[41] is reported to be beneficial for the filament stability resulting in improved endurance and retention characteristics.

Light illumination is shown to have different effect on the memristor current depending on whether the charge transport mechanism is either filament[40,41] or interface dominated.[42,43] In devices where a filament is formed (mainly originating from iodine vacancies (V_I)), light illumination leads to current suppression. This is attributed to a light-assisted ion-vacancy recombination process enabled by photo-induced halide redistribution that leads to the filament suppression and thus overall resistance increase upon illumination.[44,45] In the case of interface-dominated memristive switching, light exposure leads to an overall current enhancement that is attributed to a photogenerated electric field that lowers interface Schottky barriers driven by trapped photogenerated holes or vacancies.[42,43] **Table S2** presents a comparison among different memristors technologies in terms of switching characteristics and mechanism, while in **Table S3** a literature overview of various memristive technologies is presented in terms of multifunctionalities offered such as PV, memory, photo-memristor and -synaptic functions.

HP memristor devices can exhibit good properties with ON/OFF ratios ranging from 10 up to 10^6, but are typically higher than 10^3. The endurance and retention of these devices can be up to 10^3-10^4 cycles and 10^3-10^5 s, respectively[46]. For instance, Zhou et al. fabricated $CH_3NH_3PbI_{3-X}Cl_X$ memristors with light-tuneable switching behavior and ability to perform logic operations. The devices exhibited an ON/OFF ratio of 10^4, an endurance of 50 cycles and a retention time of $4 \cdot 10^4$s.

In addition, along with traditional oxide memristors that have shown synaptic and photo-synaptic ability[47,48], both HP and 2D material–based devices have also shown photo-synaptic abilities. In 2016, Xiao et al. reported a $MAPbI_3$-based memristor with applications in neuromorphic computing[49]. To compensate for the stability issues, the toxicity, and the environmental hazard mitigation of Pb, lead-free devices are also being employed. These low-dimensional, layered compounds ensure memristors with low operating voltages and switching yield compared to HP devices, with excellent properties and higher ON/OFF ratios compared to 3D lead-based compounds. The endurance and retention of these devices are in the range of 10^2-10^3 cycles and 10^4-10^5s, respectively.[50] Gil Kim et al. fabricated memristor devices based on 2D perovskite with an ON/OFF ratio of 10^8, an endurance and retention of 10^3 cycles and 10^4 s, respectively. Furthermore, these devices have shown synaptic behavior.[51] The wide variety and range of optoelectronic phenomena these materials portray offer immense potential to multibit memory storage and multimodal accessibility that could be utilized for neuromorphic computing. As an example of 2D material based memristors, Abnavi et. al reported a MoS_2 memristor device and photo-synapses[52]. Seo et al. fabricated an h-BN/WSe_2 optic-neural synaptic device demonstrating color-mixed pattern recognition[53].

Notably to mention, it was recently demonstrated by M. L. Cantu et al. that additives engineering in HP can be used to control shallow defects leading to optimized ion mobility and migration, hence establishing a route for efficient and highly stable PSC.[54] A hybrid photovoltaic memristor, namely an organic solar cell with inverted structure incorporating a ferroelectric transition metal oxide as electron transport layer (ETL) was demonstrated by the pioneer work of L. Cantu et al. indicating the ability to control the short circuit current (Jsc) by switching the ferroelectric polarization of the ETL.[39,55] A similar photovoltaic memristive solar cell with a planar normal structure using a perovskite active layer and a ferroelectric ETL was also reported by the same group.[56] Their work opened the path towards a light tuneable memristor, however the ferroelectric oxide requires high temperature for its synthesis– a processing incompatible with flexible substrates while also limits the PCE to low values of ~11% and requires high switching voltages (>15V).[55,56]

IoT technologies could benefit from neuromorphic flexible systems based on HP that could offer massively parallel computing within a more fault-tolerant architecture opening the path towards reducing the manufacturing cost and power consumption at the IoT edge.[5] A fully printable memristive PSC structure could therefore exhibit enhanced performance by combining features of both solar cells and memristors in a single stack, enabling light and electrical tunability at low manufacturing temperatures and being compatible with flexible substrates. In this work, we demonstrate a memristive PSC (termed as MemPVCell) fulfilling the above requirements using a quadruple cation-based perovskite. MemPVCell demonstrates a PCE of ~17% that upon appropriate memristive channel formation exhibits stable resistance switching characteristics tuneable at low voltages (<1V) without losing its PCE performance even after thousands of switching cycles. Depending on the MemPVCell layers' structure, an HRS/LRS ratio up to 10^5 was reported with a cycling endurance of >$3x10^3$ s with no apparent HRS/LRS ratio drop, and extended retention characteristics for HRS and LRS (zero and 30% change in HRS and LRS, respectively, after $3.6x10^3$ s). Parallel monitoring of MemPVCell PCE after stressful dc and ac memristive switching measurements revealed a full PCE recovery to its initial value within few minutes at rest. Lastly, basic synaptic functionalities such as STP and LTP, as well as potentiation and depreciation pulse protocols were demonstrated towards neuromorphic circuits implementation.

Experimental section

Device fabrication

Pre-patterned 2.5 × 1.5 cm^2 glass/ITO substrates (Naranjo) with a sheet resistance of ~ 20 Ω sq^{-1} were cleaned by subsequent ultrasonication in a liquid soap solution, deionized water, acetone, and isopropanol bath for 10 minutes each. The samples were dried in an oven for 30 minutes, following a UV-Ozone treatment for 20 minutes. Then, a thin layer (~ 5-10 nm) of poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA, Solaris, Mw = 20-70 kDa) from a 2mg ml^{-1} solution in toluene (Honeywell Research chemicals,≥99.7%) was spin-coated at 6000rpm for 30s. The samples were annealed at 110 ˚C for 10 minutes. The quadruple cation-based $Cs_{0.05}Rb_{0.04}(FA_{0.85}MA_{0.15})_{0.91}Pb(I_{0.85}Br_{0.15})_3$ perovskite solution was prepared by dissolving 0.2 M MABr (GreatCell Solar), 1.14 M FAI (GreatCell Solar), 0.2 M $PbBr_2$ (Alfa Aesar) and 1.24 M PbI_2 (TCI America) in 4:1 V/V anhydrous dimethylformamide (DMF) (99.8%, Sigma Aldrich):dimethyl sulfoxide (DMSO) (99.9%, Sigma Aldrich) 4:1, following the addition of 5% v/v of 1.5M CsI (Alfa Aesar) and 4% v/v of 1.5M RbI(Alfa Aesar) stock solutions in DMSO and DMF:DMSO 4:1,respectively. For the perovskite deposition, 45µl of the solution were dynamically spin-coated on the PTAA films at an angular speed of 6000 rpm for 45 s. 20 seconds prior to the end of the spinning process, the samples were washed with 200 µL of anhydrous Chlorobenzene (99.8%, Sigma Aldrich). Subsequently, the samples were annealed at 100 ˚C for 45 minutes. The $PC_{60}BM$ (99%, Solenne) electron transport layer was deposited by spin coating 45 µL of a 20 mg mL^{-1} solution in Chlorobenzene at 2000 rpm for 60s. Then, 45 µL of a 0.5 mg ml^{-1} bathocuproine solution (BCP) (96%, Sigma Aldrich) in IPA (99.5% extra dry, ACROS Organics,) were spin coated at 4000 rpm for 45 s. Finally, 100 nm Ag were deposited by thermal evaporation under a high vacuum of 10^{-6} mbar. Extended details on perovskite film formulation and characterization, as well as PSC device fabrication processing can be found in our previous reports.[32,33]

MemPVCell device characterization

The J-V characteristics of the MemPVCell devices operating as PSCs were tested in a N_2-filled glovebox using an ABB solar simulator (Oriel) equipped with a 450W Xenon lamp and a AM1.5 G filter. The intensity was calibrated at 100 mW cm^{-2} by a KG5-window Si reference cell. The J-V curves were recorded at a constant scan rate of 20 mV s^{-1} using a multiplexor test board system (Ossila), and no device preconditioning was applied before the measurements. A black metallic aperture mask was used during each measurement to fix the active area of the PSC close to 0.04 cm^2.

The external quantum efficiency (EQE) spectra were recorded using a QE-T system from Enlitech. A chopping frequency of 60 Hz was used. The calibration of the light intensity was performed using a quartz-window Si solar cell. The integrated current density was calculated by integrating the product between the spectral response of the test cell and the reference AM1.5G solar spectrum. Optoelectrical characterization was performed with a transient module of a commercially available measurement platform, ARKEO (Cicci Research s.r.l.). Spring contact probes were used to access the postsynaptic MemPVcell electrodes. Transient photovoltage (TPV) experiments were performed in small perturbation mode for a duration of 1ms by maintaining the intensity of the light pulse to less than 10% of the background voltage. The measured devices follow a mono-exponential voltage decay. Transient photocurrent (TPC) measurements were performed under large perturbations for a duration of 200 µs under a duty cycle of 0.8. For TPV and TPC measurements, the devices were connected to an external resistance of 1MΩ and 50Ω,respectively. Both the signals of open circuit voltage (for TPV) and short circuit current (for TPC) were monitored after passing them through voltage and impedance amplifiers. For the observation of the photoinduced charge extraction through linearly increasing voltage (photo-CELIV) measurements, a 470 nm fast LED source driven by 100mA current and exhibiting a Lambertian radiation pattern was used. Relaxation pulse width was set to 20 µs, charged by 50000 V s^{-1} ramp, following 13 µs delay after injection pulse. Collected signals were processed through a transimpedance amplifier and passed through a 100 MHz bandwidth digitizer running in single shot mode. EIS spectra were collected at different direct current (dc) biases varying from 0 to 1 V, while sweeping frequency from 100Hz to 1MHz.

The same setup (ARKEO) was used also for the memristive switching characteristics. For the dc switching loops, the dc voltage was swept between -1 to 1V (or higher values during the process of memristive channel formation) while measuring the current flowing through the structure at various illumination, scanning rate and the compliance current (I_{cc}) conditions. For the pulsed switching measurements, a specific pulsed memristor module was developed in collaboration with Cicci Research s.r.l, offering the option to define completely custom waveforms to be applied to the device using the convenient Arkeo waveform generator tool. In specific, arbitrarily customizable voltage pulses (either single or train of pulses) with the desired number of pulses, pulse amplitude and duration were generated and applied while monitoring the device resistance. Specific pulse protocols were defined for performing endurance and retention measurements as well as for STP, LTP and potentiation and depreciation behaviour as detailed in the corresponding plots.

RESULTS AND DISCUSSION

Structural composition and energy diagram of MemPVCell

A schematic illustration of the MemPVCell having an inverted PSC structure is shown in **Figure 1a,b** consisted of glass/ITO/PTAA/Perovskite/$PC_{60}BM$/BCP/Ag material stack. The sketch of the layers' energy diagram is graphically presented in **Figure 1c.** Hereafter, the cells using this full material stack are named MemPVCell-1. The cells without incorporating BCP interlayer are named MemPVCell-2. Finally, cells without incorporating PCBM or PTAA are named as MemPVCell-3 and MemPVCell-4, respectively.

Steady state photovoltaic characterization of MemPVCell devices

The photovoltaic performance of the MemPVCells was initially evaluated prior to performing memristive switching measurements. **Figure 2** and the corresponding tables show typical J-V characteristics and corresponding extraction of the photovoltaic parameters of 30 MemPVCell-1 and 30 MemPVCell-2 (thus with and without BCP, respectively). The statistical variation of Power conversion efficiency (PCE), fill factor (FF), short circuit current (J_{sc}) and open circuit voltage (V_{oc}) of 30 devices of each set is depicted in **Figure 2**. The J-V curves and photovoltaic parameters of the champion devices are shown in **Figure 3**. MemPVCell-1 devices exhibit an average PCE of 17.07% (champion PCE=17.97%), while devices without BCP (MemPVCell-2) demonstrate a lower PCE of 15.35% (champion PCE=16.26%). The main limiting factor of MemPVCell-2 is reported to be the lower FF values associated to the less ohmic contact between Ag and PCBM in the absence of BCP - an insulating layer that helps in avoiding related Schottky barriers at metal semiconductor interfaces.[32,33] Despite the lower PCE of MemPVCell-2 devices, the absence of BCP is reported to be beneficial for the memristive switching properties as it will be shown later in the manuscript.

Transient photovoltaic characterization of MemPVCell

Transient photovoltage (TPV), TPC, Photo-CELIV and EQE measurements were performed in a typical MemPVCell-1 device and plotted in **Figure S1, S2, S3 and S4**, respectively. Small perturbation TPV decays followed a single exponential trend, which can result from either a charge carrier annihilation or a three-body recombination. Since the excitons in perovskites dissociate after 2 ps upon generation and our measurement cover a µs-scale, we can safely disregard the potential exciton contribution.[32,33] Hence, the measured decay curves are the consequence of the electron-hole recombination, and the transient tail can directly yield the carrier lifetimes. The carrier lifetimes (~5 µs) were extracted

from corresponding transient tail of TPV decay curves (**Fig. S1**) that follow a single exponential trend.

The TPC measurements were performed in high perturbation regime (0.8 duty cycle) and show the absence of deep trap states in all the tested samples **(Figure S2)**. The drift mobility of electrons/holes was probed using charge extraction by linearly increasing voltage (photo-CELIV) under various light pulse delay points. More in detail, the drift mobility was derived from the extracted charge represented by the part of the transient superimposed over the displacement current level (**Figure S3**). Taking into account the fact that perovskites are not highly disordered materials and according to the equation proposed by Lorrmann et al. mobility can be derived:[57]

$$\mu = \frac{L}{2At_{max}^2}\left[\frac{1}{6.2(1+0.002\frac{\Delta I}{I_0})}+\frac{1}{(1+0.12\frac{\Delta I}{I_0})}\right]^2$$

, where L is active layer thickness, A is the ramp of the extraction voltage, t_{max} is the point of transient measurement where current reaches its peak and $\Delta I/I_0$ ratio corresponds to the level of charge accumulation. Notably, the delay of the photogeneration pulses does not affect the drift mobility, which means that the charge carrier transport is well balanced.

Fig. S4 shows the EQE spectrum of a typical device together with the calculated current density, which matches the Jsc value extracted from J-V curves. **Fig. S5** depicts typical EIS data of MemPVCell-1 before the memristive channel formation, at different direct current (dc) biases varying from 0 to 1 V, while sweeping the frequency from 100Hz to 1MHz. In all cases, standard EIS arcs appear showing that the series resistance is decreasing as the dc bias increases. In the next section, we will discuss EIS data in HRS and LRS state after forming the memristive channel.

Resistance switching characteristics of MemPVCell devices

Figure 4 shows dc voltage sweeps of the MemPVCell-1 device by varying the memristive channel forming process through setting different values of compliance current, Icc (1 and 10mA).[27,35] Moreover, different voltage scanning rates (10mV/s, 50mV/s, 100mV/s) were tested to identify how these parameters affect the V_{set} and V_{reset} values as well as the ON/OFF ratio (**Table 1**).[35] The memristive channel in a pristine sample was achieved by applying a positive voltage exceeding the required threshold of ~ 2V. The dc voltage was applied to the Ag top electrode, while the ITO bottom electrode was grounded for all relevant measurements.

Stable bipolar resistive switching loops were obtained for each of tested conditions with an ON/OFF ratio ranging between 10^3 to 10^5, while a low (~100-200mV) positive voltage, V_{set}, results to HRS to LRS transition. The HRS is restored upon exceeding a moderate (~700mV) negative voltage threshold, V_{reset}. **Table 1** summarizes the MemPVCell-1's ON/OFF ratio, V_{set} and V_{reset} dependence on scanning rate and I_{cc}. The general trend is that V_{set} and V_{reset} are increasing as scanning rate or I_{cc} increase with a bigger influence on V_{reset}.[35] ON/OFF ratio is also increasing at high I_{cc} values, reaching a value up to 10^5. Targeting high ON/OFF ratio, initial high barriers between the active layer and the electrodes are reported in the majority of HP-based memristors[34-38] by avoiding the insertion of electron and hole transport layers in structure. Although this is route of memristive performance improvement, however at a cost of high power and voltage operation, these energy barriers also render these structures incompatible to efficient solar energy harvesting.

Figure 5 presents the statistical distribution of 15 different MemPVCell-1 and 15 different MemPVCell-2 devices measured at scanning rate and I_{cc} conditions of 10mV/s and 10mA, respectively. It is apparent that MemPVCell-1 compared to MemPVCell-2 devices, exhibit a slightly higher V_{set} (~0.15±0.06V compared to 0.13±0.04V) while having a slightly lower V_{reset} (-0.65±0.10V compared to -0.75±0.06V). Overall, MemPVCell-2 exhibits less variation in resistive switching voltages measured among multiple cells of the same type (**Table S4). Figure S6** depicts up to 125 consecutive dc resistance switching loops for both MemPVCell-1 (**Fig. S6a**) and MemPVCell-2 (**Fig. S6b**) devices revealing that both devices have excellent resistance states stability.

Mechanism and light tuning of resistance switching characteristics

After analyzing the DC resistive switching behavior of the MemPVCell devices, it is crucial to examine whether the underlying mechanism responsible for the resistive switching is filament-based (either Ag or V_I migration) or interface dominated. The proposed mechanism for MemPVCell is the formation/rupture of V_I enabled filaments[40,41,44,45] that is based on two arguments: The first argument lies in the abrupt increase\decrease of current by orders of magnitude after exceeding the switching threshold (SET/RESET process), under DC voltage sweeps. Nevertheless, this argument only precludes the interfacial switching case and cannot distinguish whether the filament originates in Ag or halide vacancies in the perovskite active layer or a combination of both. The second argument is presented in **Figure 6**. In this measurement, consecutive identical pulses of increasing light illumination were applied to the as-formed MemPVCell-1 device. In **Figure 6 a**, consecutive pulses of 1V amplitude and 10ms width were applied for light intensities of 8,16,25,40,60 and 80 mW/cm^2, respectively. The resistance of MemPVCell-1 increases with increasing light intensity and eventually approaches the HRS state, indicating the rupture of V_I filaments enabled by photo-induced halide (Iodine) redistribution.[44,45] Increasing the pulse width (1V,100ms) in **Figure 6b** minimizes the light induced resistance enhancement although cannot prevent the device resistance to increase approaching 1000ohms. On the other hand, increasing the pulse amplitude at 2V (width either 10ms, **Figure 6c**, or 50ms, **Figure 6d** does have a stronger impact on

device LRS by setting its initial value below 100 ohm at dark conditions (in contrast with 1V pulse case where the LRS at dark conditions is about 300 ohm). It is noted that even under 76mW/cm^2 light illumination the LRS lies around 300 ohm. Overall, the higher pulse amplitude leads to a stronger filament formation thus to a lower LRS value (both at dark and light conditions) a situation that opposes the rupture of V_I filaments and compensates for the effect of light on the active layer. Finally, increasing the pulse width from 10ms to 50ms under the same amplitude of 2V further stabilizes the LRS to lower values while makes its light tunability range to lie between 70-130 ohm under dark and 76mW/cm^2, respectively. This light controlled LRS value could open the path for analogue computing processes apart from digital neuromorphic circuits applications. Similar behavior was observed for the case of MemPVCell-2.

We then investigated the effect of light illumination on the DC resistive switching of MemPVCell-1. Corresponding dc switching measurements under light illumination of 50mW/cm^2 are presented in **Figure S7. Table S5a** also shows the V_{set} and V_{reset} voltage values for light intensities of 8 and 16mW/cm^2. It is noted that under light, the V_{set} increases while the V_{reset} becomes less negative indicating that light-generated carriers prevent the transition from HRS to LRS while assist the opposite transition from LRS to HRS enabled by a light-modulated carriers' barrier.[40,42,58,59] The same trend is evident in **Table S5b**, showing the dependence of V_{set} and V_{reset} as a function of scan rate. As the scan rate decreases, the set voltage significantly decreases, meaning that prolonged light illumination assists the reset process and the rupture of V_I filaments. Similarly, the set voltage is reduced for decreasing scan rate, as the prolonged electric field application reduces the switching threshold to LRS under illumination. Our results are in agreement with photo-induced iodide redistribution[44] and annihilation of Frenkel defects[45] that were shown to lead to current suppression under light illumination in HP memristors.[60] In particular, these measurements verify the existence of iodine filaments as the primary mechanism responsible for resistive switching indicating that the increase/decrease of device conductance is attributed to the increase/decrease of V_I·/V_I× concentration. Contribution from Ag migration cannot be also excluded. Similar behavior was observed for the case of MemPVCell-2.

Finally, we have investigated how the EIS spectra are affected (**Figure S8)** by applying a dc bias and sweeping it across the V_{set} threshold of ~150mV. The sample is initialized at HRS at zero bias while when the bias is above 0.1V, a transition from an arch-shaped spectra to an almost vertical line is observed indicating the gradual transition to LRS.[61]

Endurance and retention characteristics of MemPVCell devices

To investigate further the HRS and LRS stability, we have implemented standard states endurance and retention measurements using ac pulses for both types of samples.[24-28] **Figure 7** depicts thousands of HRS to LRS cycling loops indicating the overall high endurance of MemPVCell-1 and -2 devices. For these measurements we have used a large number of ac pulses up to 3x10^3 cycles having pulse amplitude of ±1V and duration of 100ms. Both devices exhibit a zero change in HRS/LRS ratio even after 3x10^3 switching cycles. The purple shadow around the data points reflects the variation of thousands of switching pulses revealing the high stability of the HRS and LRS states under fast ac excitations. For the specific pulses' configuration, MemPVCell-1 shows an initial HRS/LRS ratio of ~10^3, while MemPVCell-2 has a value of ~ 10^4 indicating the beneficial role on switching characteristics when BCP is not included in the structure. This is directly related to Schottky barriers development when BCP is absent in the device that results in less current conduction and thus higher HRS values. Overall, the high endurance of MemPVCell devices is likely linked to the mutli-cation nature of the quadruple perovskite and especially to the beneficial role of Rb and the supressed MA contribution. [41]

Moreover, retention characteristics of HRS and LRS states for both MemPVCell-1 and -2 are presented in **Figure 8**. Initial HRS was set by applying a pulse with amplitude of 1V and duration of 100ms, while the LRS was set by applying a pulse with amplitude of -1V. The HRS demonstrates a superior retention showing no change even after of 3500s for both types of samples. On the other hand, LRS exhibits a gradually increase of the initial value (~200ohm) with time. In the case of MemPVCell-1**,** after ~1300s we observe a sudden, permanent switch from LRS to HRS. Notably, MemPVCell-2 exhibits a much better stability of LRS with time resulting in 30% resistance increase after 3500s. Overall, the HRS/LRS ratio of MemPVCell-2 depicts a retention of more than 70% of its initial value while MemPVCell-1 retains only 10% of its initial value after 3500s. Therefore, MemPVCell-2 device structure offer much-improved LRS retention behaviour that results also in higher HRS/LRS ratio retention. The retention of MemPVCell-1 was also studied for ±2V pulse amplitude. In this case, the ON/OFF ratio reduced to 100, compared to the 1V case. The results are shown in **Table S6**.

Correlation between PCE performance and memristive switching

The key advantage of the proposed MemPVCell structure is the ability to use the same material stack for parallel solar energy harvesting and neuromorphic computation tasks going beyond von Neumann architectures. To investigate how the initial PCE performance of the MemPVCell prior to memristive channel formation is affected by the resistance switching loops, we have plotted in **Figure 9a**, corresponding characteristics in pristine cells, after 50 and 100 switching loops for both MemPVCell-1 and MemPVCell-2. After 100 consecutive dc switching loops, the PCE of MemPVCell-1 remains at 92% of its initial value, whereas MemPVCell-2 retains 96% its PCE value even after 125 switching loops. For both samples, the stressful process of memristive switching loops didn't affect significantly the PCE performance, while MemPVCell-2 exhibits a faster recovery process. To investigate how the ac switching excitations also affect the PCE performance, in **Figure 9b** we plot how the PCE of the MemCell-1 is recovered with

time after pulsed endurance tests. Specifically, we continuously monitor the PCE of the device in time after performing 3000 endurance cycles. We report that the PCE is significantly dropped immediately after these stressful excitations, however a quick recovery is observed within a timeframe of few minutes.

Neuromorphic behavior of MemPVCell devices

To validate further the memristive performance of the MemPVCell, we have measured basic synaptic functionalities by applying potentiation and depreciation pulse protocols at different pulse and light illumination conditions (**Figure 10a,b**) as well as measure STP/LTP effects.[10-15,24-28] For the potentiation and depreciation protocols at dark conditions, and when the memristor is set close to LRS (**Fig. 10a**) , we used a sequence of 50 pulses with amplitude of 300mV and 50 pulses at -300mV with a duration of 10ms each. During the first positive 50 pulses, a continuous increase of current is reported, while during the rest 50 negative pulses the opposite behaviour is observed in line with potentiation and depreciation of conventional memristors. [24-28] For the measurements of **Fig.10b**, we applied 30 pulses at +700mV and 30 pulses at -600mV with duration of 1ms each pulse at different light illumination of 25-50mW/cm^2 (**Fig. 10b**). Light excitation results in enhanced current amplitude following an almost linear dependence.[26,27] In **Figure 10c**, we demonstrate typical STP and LTP synaptic behaviours by implementing specific train pulses, while the device is initialized in the HRS. For the STP process, 4 consecutive pulses of 100mV in amplitude and 2ms in duration were applied, while the current is afterwards recorded in time. This train of moderate pulses results in an initial increase of current (~10μA) for a period of 100 s, whereas afterwards the devices is spontaneously switched back to HRS. On the contrary, by applying 5 consecutive pulses of 700mV in amplitude and 5ms in duration, we observed the direct transition of the sample to LRS and its stability in this state for a period of 400 s demonstrating therefore a LTP process. As a demonstration of mimicking a spike-timing dependent plasticity (STDP) based on MemPVCell, in **Figure 11** the effect of a train of 10 pulses (-600mV amplitude, 5ms duration) on synaptic current is depicted with different time interval between them being either 500ms (**Fig. 11a**) or 5ms (**Fig. 11b**). In case the pulses are well separated in time, no effect on current is reported. On the other hand, when the time interval is within few ms, a clear STDP effect is observed resulting in a 4x enhancement of synaptic current.

Routes towards further device performance improvement were investigated by modifying the layer components of the MemPVCell-1 structure. Specifically, we prepared samples without including PCBM layer, termed as MemPVCell-3 (**Figure S9**), and samples without including PTAA layer (MemPVCell-4 structure, **Figure S10**). In both cases, the memristive performance was worse compared to MemPVCell-1 and -2, while the PCE performance was significantly suppressed (PCE less than 5%) - as expected in a PSC structure without electron transport layer (MemPVCell-3) or without hole transport layer (MemPVCell-4). MemPVCell-3 required higher V_{set} and V_{reset} pulses, while the HRS/LRS ratio is reported to be 2 orders of magnitude less compared to MemPVCell-1 and MemPVCell-2. Notably to mention, only very few devices of the same batch exhibited memristive switching characteristics. MemPVCell-4 required high switching voltages while only few devices were operational (this is probably attributed to the low perovskite quality when is coated on ITO instead of the PTAA layer), despite the good stability of the working devices.

Conclusions

In this study, we demonstrated that is possible to use an efficient inverted PSC structure based on a quadruple cation-based perovskite (this the first memristor realization based on quadruple cation perovskite at least to the best of the authors knowledge), and implement, using the same material stack, parallel solar energy harvesting and memristive functionalities. We show that a PSC with an average PCE of ~17% is capable, upon appropriate memristive channel formation, to demonstrate stable resistance switching characteristics without losing its PCE performance even after multiple dc or thousands of ac switching cycles. Specifically, the MemPVCell demonstrates HRS to LRS ratio of up to 10^5, fast and light-tuneable switching cycles with endurance of $3x10^3$ with no detectable HRS/LRS ratio drop. Overall, an HRS/LRS ratio retention of up to 3600sec with less than 30% drop of its initial value was also shown for MemPVCell-2. Corresponding PCE performance was also monitored after the implementation of multiple resistance switching loops and endurance cycles indicating that a full PCE recovery to device initial value is attainable within few minutes of rest. Aiming at improving further the device performance, modifications of MemPVCell's layered structure were investigated, a process that allowed to identify each layer impact on the parallel photovoltaic and memristive switching characteristics. This process suggests that the interfaces between the perovskite and PCBM, as well as PCBM and Ag contact, are vital for the good overall performance of the MemPVCell. On-going experiments focus on developing novel interfacial engineering routes and are expected to allow achieving much better memristive performance (increasing HRS/LRS ratio, endurance, and retention) without sacrificing the PCE performance.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work has been supported by European Union's Horizon 2020 research and innovation program under project EMERGE. The EMERGE project has received funding under grant agreement Nº 101008701.

Notes and references

1 S. Bains, *Nat Electron*, 2020, **3**, 348–351.

2 Wm. A. Wulf and S. A. McKee, *SIGARCH Comput. Archit. News*, 1995, **23**, 20–24.

3 M. A. Zidan, J. P. Strachan and W. D. Lu, *Nat Electron*, 2018, **1**, 22–29.

4 H. Yasuura, C.-M. Kyung, Y. Liu and Y.-L. Lin, Eds., *Smart Sensors at the IoT Frontier*, Springer International Publishing, Cham, 2017.

5 Q. Xia and J. J. Yang, *Nat. Mater.*, 2019, **18**, 309–323.

6 F. Zhou, Z. Zhou, J. Chen, T. H. Choy, J. Wang, N. Zhang, Z. Lin, S. Yu, J. Kang, H.-S. P. Wong and Y. Chai, *Nat. Nanotechnol.*, 2019, **14**, 776–782.

7 F. Cai, J. M. Correll, S. H. Lee, Y. Lim, V. Bothra, Z. Zhang, M. P. Flynn and W. D. Lu, *Nat Electron*, 2019, **2**, 290–299.

8 R. Berdan, T. Marukame, K. Ota, M. Yamaguchi, M. Saitoh, S. Fujii, J. Deguchi and Y. Nishi, *Nat Electron*, 2020, **3**, 259–266.

9 S. Nau, C. Wolf, S. Sax and E. J. W. List-Kratochvil, *Adv. Mater.*, 2015, **27**, 1048–1052.

10 P. C. Harikesh, B. Febriansyah, R. A. John and N. Mathews, *MRS Bull.*, 2020, **45**, 641–648.

11 Y. Tuchman, T. N. Mangoma, P. Gkoupidenis, Y. van de Burgt, R. A. John, N. Mathews, S. E. Shaheen, R. Daly, G. G. Malliaras and A. Salleo, *MRS Bull.*, 2020, **45**, 619–630.

12 Y. van de Burgt, A. Melianas, S. T. Keene, G. Malliaras and A. Salleo, *Nat Electron*, 2018, **1**, 386–397.

13 J. Y. Gerasimov, D. Zhao, A. Sultana, T. Abrahamsson, S. Han, D. Bliman, D. Tu, D. T. Simon, R. Olsson, X. Crispin, M. Berggren and S. Fabiano, *Adv. Electron. Mater.*, 2021, **7**, 2001126.

14 D. D. A. Koutsouras, T. Prodromakis, G. G. Malliaras, P. W. M. Blom and D. P. Gkoupidenis, 2019, 9.

15 F. Torricelli, D. Z. Adrahtas, Z. Bao, M. Berggren, F. Biscarini, A. Bonfiglio, C. A. Bortolotti, C. D. Frisbie, E. Macchia, G. G. Malliaras, I. McCulloch, M. Moser, T.-Q. Nguyen, R. M. Owens, A. Salleo, A. Spanu and L. Torsi, *Nat Rev Methods Primers*, 2021, **1**, 66.

16 G. Kakavelakis, M. Gedda, A. Panagiotopoulos, E. Kymakis, T. D. Anthopoulos and K. Petridis, *Advanced Science*, 2020, **7**, 2002098.

17 G. Kakavelakis, E. Gagaoudakis, K. Petridis, V. Petromichelaki, V. Binas, G. Kiriakidis and E. Kymakis, *ACS Sensors*, 2018, **3**, 135–142.

18 C.-X. Zhang, T. Shen, D. Guo, L.-M. Tang, K. Yang and H.-X. Deng, *InfoMat*, 2020, **2**, 1034–1056.

19 Q. Liao, X. Jin and H. Fu, *Advanced Optical Materials*, 2019, **7**, 1900099.

20 H. Wang and D. H. Kim, *Chemical Society Reviews*, 2017, **46**, 5204–5236.

21 X. Liu, D. Yu, X. Song and H. Zeng, *Small*, 2018, **14**, 1801460.

22 K. Rogdakis, N. Karakostas and E. Kymakis, *Energy Environ. Sci.*, 2021, **14**, 3352–3392.

23 Z. Fan, K. Sun and J. Wang, *Journal of Materials Chemistry A*, 2015, **3**, 18809–18828.

24 X. Xiao, J. Hu, S. Tang, K. Yan, B. Gao, H. Chen and D. Zou, *Adv. Mater. Technol.*, 2020, **5**, 1900914.

25 G. Cao, C. Cheng, H. Zhang, H. Zhang, R. Chen, B. Huang, X. Yan, W. Pei and H. Chen, *J. Semicond.*, 2020, **41**, 051205.

26 R. A. John, N. Shah, S. K. Vishwanath, S. E. Ng, B. Febriansyah, M. Jagadeeswararao, C.-H. Chang, A. Basu and N. Mathews, *Nat Commun*, 2021, **12**, 3681.

27 U. Das, P. Sarkar, B. Paul and A. Roy, *Appl. Phys. Lett.*, 2021, **118**, 182103.

28 Y. Fang, S. Zhai, L. Chu and J. Zhong, *ACS Appl. Mater. Interfaces*, 2021, **13**, 17141–17157.

29 X. Zhao, H. Xu, Z. Wang, Y. Lin and Y. Liu, *InfoMat*, 2019, inf2.12012.

30 M. Saliba, T. Matsui, K. Domanski, J. Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J. P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Science*, 2016, **354**, 206–209.

31 M. Petrović, K. Rogdakis and E. Kymakis, *J. Phys. Energy*, 2019, **1**, 044001.

32 D. Tsikritzis, K. Rogdakis, K. Chatzimanolis, M. Petrović, N. Tzoganakis, L. Najafi, B. Martín-García, R. Oropesa-Nuñez, S. Bellani, A. E. Del Rio Castillo, M. Prato, M. M. Stylianakis, F. Bonaccorso and E. Kymakis, *Mater. Adv.*, 2020, **1**, 450–462.

33 K. Chatzimanolis, K. Rogdakis, D. Tsikritzis, N. Tzoganakis, M. Tountas, M. Krassas, S. Bellani, L. Najafi, B. Martín-García, R. Oropesa-Nuñez, M. Prato, G. Bianca, I. Plutnarova, Z. Sofer, F. Bonaccorso and E. Kymakis, *Nanoscale Adv.*, 2021, **3**, 3124–3135.

34 E. J. Yoo, M. Lyu, J. H. Yun, C. J. Kang, Y. J. Choi and L. Wang, *Advanced Materials*, 2015, **27**, 6170–6175.

35 Y. Huang, L. Tang, C. Wang, H. Fan, Z. Zhao, H. Wu, M. Xu, R. Shen, Y. Yang and J. Bian, *ACS Applied Electronic Materials*, 2020, **2**, 3695–3703.

36 X. F. Cheng, W. H. Qian, J. Wang, C. Yu, J. H. He, H. Li, Q. F. Xu, D. Y. Chen, N. J. Li and J. M. Lu, *Small*, 2019, **15**, 1905731.

37 D. Liu, Q. Lin, Z. Zang, M. Wang, P. Wangyang, X. Tang, M. Zhou and W. Hu, *ACS Applied Materials and Interfaces*, 2017, **9**, 6171–6176.

38 W. H. Qian, X. F. Cheng, Y. Y. Zhao, J. Zhou, J. H. He, H. Li, Q. F. Xu, N. J. Li, D. Y. Chen and J. M. Lu, *Advanced Materials*, 2019, **31**, 1806424.

39 A. Pérez-Tomás, *Adv. Mater. Interfaces*, 2019, **6**, 1900471.

40 X. Zhu, J. Lee and W. D. Lu, *Advanced Materials*, 2017, **29**, 1700527.

41 S. Lee, J. Choi, J. B. Jeon, B. J. Kim, J. S. Han, T. L. Kim, H. S. Jung and H. W. Jang, *Adv. Electron. Mater.*, 2019, **5**, 1800586.

42 X. Guan, W. Hu, M. Azimul Haque, N. Wei, Z. Liu, A. Chen, T. Wu, X. Guan, W. J. Hu, M. A. Haque, Z. Liu, A. Chen, T. Wu and N. Wei, *Advanced Functional Materials*, 2018, **28**, 1704665.

43 S. Ham, S. Choi, H. Cho, S.-I. Na and G. Wang, *Adv. Funct. Mater.*, 2019, **29**, 1806646.

44 D. W. deQuilettes, W. Zhang, V. M. Burlakov, D. J. Graham, T. Leijtens, A. Osherov, V. Bulović, H. J. Snaith, D. S. Ginger and S. D. Stranks, *Nat Commun*, 2016, **7**, 11683.

45 E. Mosconi, D. Meggiolaro, H. J. Snaith, S. D. Stranks and F. De Angelis, *Energy Environ. Sci.*, 2016, **9**, 3180–3187.

46 X. Xiao, J. Hu, S. Tang, K. Yan, B. Gao, H. Chen and D. Zou, *Advanced Materials Technologies*, 2020, **5**, 1–29.

47 A bioinspired optoelectronically engineered artificial neurorobotics device with sensorimotor functionalities | Nature Communications, https://www.nature.com/articles/s41467-019-11823-4, (accessed June 19, 2022).

48 M. Lanza, H.-S. P. Wong, E. Pop, D. Ielmini, D. Strukov, B. C. Regan, L. Larcher, M. A. Villena, J. J. Yang, L. Goux, A. Belmonte, Y. Yang, F. M. Puglisi, J. Kang, B. Magyari-Köpe, E. Yalon, A. Kenyon, M. Buckwell, A. Mehonic, A. Shluger, H. Li, T.-H. Hou, B. Hudec, D. Akinwande, R. Ge, S. Ambrogio, J. B. Roldan, E. Miranda, J. Suñe, K. L. Pey, X. Wu, N. Raghavan, E. Wu, W. D. Lu, G. Navarro, W. Zhang, H. Wu, R. Li, A. Holleitner, U. Wurstbauer, M. C. Lemme, M. Liu, S. Long, Q. Liu, H. Lv, A. Padovani, P. Pavan, I. Valov, X. Jing, T. Han, K. Zhu, S. Chen, F. Hui and Y. Shi, *Adv. Electron. Mater.*, 2019, **5**, 1800143.

49 Z. Xiao and J. Huang, *Advanced Electronic Materials*, 2016, **2**, 1600100.

50 Y. Fang, S. Zhai, L. Chu and J. Zhong, *ACS Applied Materials & Interfaces*, 2021, **13**, 17141–17157.

51 S. Gil Kim, Q. Van Le, J. Su Han, H. Kim, M.-J. Choi, S. A. Lee, T. Ludvic Kim, S. Bum Kim, S. Young Kim, H. Won Jang, S. G. Kim, J. S. Han, H. Kim, M. Choi, S. A. Lee, T. L. Kim, S. B. Kim, H. W. Jang, Q. Van Le, D. Nang and V. S. Y Kim, *Advanced Functional Materials*, 2019, **29**, 1906686.

52 A. Abnavi, R. Ahmadi, A. Hasani, M. Fawzy, M. R. Mohammadzadeh, T. De Silva, N. Yu and M. M. Adachi, *ACS Appl. Mater. Interfaces*, 2021, **13**, 45843–45853.

53 S. Seo, S.-H. Jo, S. Kim, J. Shim, S. Oh, J.-H. Kim, K. Heo, J.-W. Choi, C. Choi, S. Oh, D. Kuzum, H.-S. P. Wong and J.-H. Park, *Nat Commun*, 2018, **9**, 5106.

54 H. Xie, Z. Wang, Z. Chen, C. Pereyra, M. Pols, K. Gałkowski, M. Anaya, S. Fu, X. Jia, P. Tang, D. J. Kubicki, A. Agarwalla, H.-S. Kim, D. Prochowicz, X. Borrisé, M. Bonn, C. Bao, X. Sun, S. M. Zakeeruddin, L. Emsley, J. Arbiol, F. Gao, F. Fu, H. I. Wang, K.-J. Tielrooij, S. D. Stranks, S. Tao, M. Grätzel, A. Hagfeldt and M. Lira-Cantu, *Joule*, 2021, **5**, 1246–1266.

55 A. Pérez-Tomás, A. Lima, Q. Billon, I. Shirley, G. Catalan and M. Lira-Cantú, *Adv. Funct. Mater.*, 2018, **28**, 1707099.

56 A. Pérez-Tomas, H. Xie, Z. Wang, H.-S. Kim, I. Shirley, S.-H. Turren-Cruz, A. Morales-Melgares, B. Saliba, D. Tanenbaum, M. Saliba, S. M. Zakeeruddin, M. Gratzel, A. Hagfeldt and M. Lira-Cantu, *Sustainable Energy Fuels*, 2019, **3**, 382–389.

57 J. Lorrmann, B. H. Badada, O. Inganäs, V. Dyakonov and C. Deibel, *Journal of Applied Physics*, 2010, **108**, 113705.

58 F. Zhou, Y. Liu, X. Shen, M. Wang, F. Yuan and Y. Chai, *Adv. Funct. Mater.*, 2018, **28**, 1800080.

59 S.-Y. Cai, C.-Y. Tzou, Y.-R. Liou, D.-R. Chen, C.-Y. Jiang, J.-M. Ma, C.-Y. Chang, C.-Y. Tseng, Y.-M. Liao, Y.-P. Hsieh, M. Hofmann and Y.-F. Chen, *ACS Appl. Mater. Interfaces*, 2019, **11**, 4649–4653.

60 X. Zhu and W. D. Lu, *ACS Nano*, 2018, **12**, 1242–1249.

61 C. Gonzales, A. Guerrero and J. Bisquert, *Appl. Phys. Lett.*, 2021, **118**, 073501.