

Green energy by recoverable triple-oxide mesostructured perovskite photovoltaics

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Perovskite solar cells have developed into a promising branch of renewable energy. A combination of feasible manufacturing and renewable modules can offer an attractive advancement to this field. Herein, a screen-printed three-layered all-nanoparticle network was developed as a rigid framework for a perovskite active layer. This matrix enables perovskite to percolate and form a complementary photoactive network. Two porous conductive oxide layers, separated by a porous insulator, serve as a chemically stable substrate for the cells. Cells prepared using this scaffold structure demonstrated a power conversion efficiency of 11.08% with a high open-circuit voltage of 0.988 V. Being fully oxidized, the scaffold demonstrated a striking thermal and chemical stability, allowing for the removal of the perovskite while keeping the substrate intact. The application of a new perovskite in lieu of a degraded one exhibited a full regeneration of all photovoltaic performances. Exclusive recycling of the photoactive materials from solar cells paves a path for more sustainable green energy production in the future.

perovskite solar cells | sustainability | environmental science

 $\mathbf{E}_{(1)}^{\text{levating world temperatures along climatic model predictions}$ green renewable energy production. On the photovoltaic branch, organic (2), inorganic (3, 4), and photosynthetic (5) light harvesters were investigated extensively. In recent years, organic-inorganic perovskite solar cells (PSCs) have been breaking efficiency records (6). Perovskites are a widely diverse and tunable class of materials (7), possessing high charge diffusion length characteristics under illumination. The attractive qualities and surge of development have made the PSCs, especially fully printable panels (8), prominent candidates for large-scale commercialization (9). Simultaneously, much effort has been made to stabilize perovskite's intrinsic properties (10) through the research of different compositions and fabrication methods. These efforts include the introduction of hole conductor-free configurations (11), two-dimensional perovskite compositions (12), and, recently, the usage of methylammoniumfree compounds (13). In a typical PSC structure, the perovskite layer is situated between an electron-transporting layer (ETL) on the one side and a hole-transporting material (HTM) on the other side. Traditionally, a metal contact is evaporated onto the HTM as a cathode, sealing the basic functional structure of the cell. The alignment of the electronic structure of the functional layers enables the ETL to effectively block the diffusion of holes from the perovskite and the HTM to block electrons from reaching the cathode. HTM-free configurations eliminate the HTM layer between the light absorber and the cathode and rely on the ETL alone to induce anisotropic average diffusion of the charges as a photocurrent. Since HTMs are commonly expensive and prone to degradation over time, HTM-free configurations contribute to the cells' durability and tenability and significantly lower their cost. One such configuration utilizes a porous carbon layer as the cathode of the cell (14), allowing the perovskite precursor solution to percolate through the pores and crystalize inside the structure.

Here, a triple-layered structure of sintered nanoparticles (NPs) was designed as a general scaffold for various perovskite compositions and deposition methods. The rigid and stable, screen-printed

oxide nanoparticle films form layers which manifest electronic attributes similar to their building blocks. The general structure of the scaffold includes a porous electron-conducting NP layer and a porous NP cathode, separated by a porous insulating NP layer. Though the use of alternative conductive NPs is plausible, indium tin oxide (ITO) particles were chosen as the cathodic material in this work. This conductive metal oxide material can endure more extreme chemical and thermal conditions than most other nanoparticles can. The virtue of such oxides lies in their strong structure and inert chemical behavior toward oxygen and water. NPs of the closely related metal oxide fluorine-doped tin oxide (FTO) are possible candidates for the substitution of ITO as the cathodic material in the future, with economic advantages appealing for commercialization. Widely used in the field of PSCs, mesoporous TiO_2 (mpTiO_2) possesses the ability to efficiently receive and conduct electrons from the conduction band of the perovskite and thus serves as the ETL in the structure. Since charge separation in PSCs arises from light absorption in the perovskite, continuity and connectivity of the perovskite material must be maintained, along with complete insulation between the anodic and cathodic parts of the cell. Screen-printed mesoporous ZrO₂ (mpZrO₂) was used here as an ideal material choice for the insulating layer. All three mentioned layers were successively printed and sintered atop a transparent FTO-coated glass photoanode to complete a full scaffold configuration of FTO/mpTiO2/mpZrO2/mpITO. The perovskite solution can then be applied directly onto the cathode contact, subsequently forming a three-dimensional polycrystalline network

Significance

In the progress toward a more sustainable world, wind and solar energy production are the leading renewable contenders. The emerging field of perovskite solar cells has achieved remarkable efficiencies and is gaining a steady foothold among other solar technologies. However, a worldwide deployment of perovskite solar panels poses environmental and economic problems due to degradation over time. The degrading photoactive materials are usually situated between other layers, complicating or inhibiting cell recycling. Here, we investigated a structure for perovskite solar cells composed of chemically and thermally stable oxides which includes the application of the photoactive perovskite material as a final step. This structure allows for the removal and replacement of degraded perovskite, with a full restoration of photovoltaic characteristics.

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of perovskite in the cavities between the scaffold NPs. The ITO contact provides direct electron injection to the perovskite under illumination, and at this point the cell's full structure is complete, without the need for any additional steps. Here, the deposition of (MA_{0.15}FA_{0.85})PbI₃ perovskite is demonstrated, along with an optical, morphological, electronic, and photovoltaic characterization of the cells. These scalable solar cells exhibited high short-circuit currents, impressive stability, and the unique possibility of recycling by removing and reapplying damaged or degraded perovskite.

Results and Discussion

The Structure and Properties of Triple-Oxide PSCs. One important aspect of this triple-oxide mesostructure is its immense interface and the nanostructured perovskite network that may crystalize within its cavities. This large interface may serve to compensate for the lack of the almost single-crystal pathway between the HTM and ETL, seen in the standard layered PSCs configurations. We chose ITO NPs to be the cathodic top contact for our recyclable all-NP mesoporous perovskite solar cells. ITO is a conductive, rigid, and transparent metal oxide used for versatile photoelectronic applications. Therefore, it was expected to render some of these qualities to a mesoporous thin film of sintered ITO nanocrystals (15). To be implemented in the cell structure, commercially available 50 nm ITO nanopowder was processed into a smooth-textured paste suitable for screen printing. A procedure reported initially for titanium dioxide paste by Ito et al. (16) was modified and utilized to prepare the ITO paste. The printed paste yielded mesoporous ITO films with a thickness on the micrometer scale. Sintering temperatures of 600 °C allowed maximal conductivity of the film without compromising the other components of the cell. The Hall effect measurement of such a film, on a glass substrate, revealed a sheet resistivity of 180.5 Ω /sq (ohms per square) and carrier concentration of 8.7×10^{19} cm⁻³.

The entire solar cell is fabricated using scalable printing techniques, and its basic structure is illustrated in Fig. 1*A*. The foundation of the cell, on top of which all functional layers are deposited, is a conductive FTO-coated glass. Following the application of a compact TiO₂, a mesoporous TiO₂ film was screen printed on the substrate, using a 20 nm diameter NP paste. An insulating mpZrO₂ was then printed on top of the mpTiO₂ using a 30 nm diameter NP paste. Thereafter, the printing of ITO on top of the mpZrO₂ marks the final step in the construction of the





Fig. 1. Device architecture and physical, optical, and electronic characterizations. (A) Illustration of the FTO/mpTiO₂/mpZrO₂/mpITO cell design. The triplelayered oxide nanoparticle matrix is interweaved with a complimentary perovskite network which has crystalized within its cavities. Upon illumination, charge separation in the perovskite generates anodal and cathodal photocurrents in the FTO and ITO, respectively. (*B*) Illustration (*Left*) and scanning electron microscope image (*Right*) of a cell cross-section, presenting the arrangement of ITO, ZrO₂, TiO₂ (porous and compact), and FTO functional layers atop a glass substrate as well as the penetration of perovskite through the porous layers. (C) Absorbance spectra of the cell scaffold not including ITO (curve 1), including ITO (curve 1), and including ITO and FA_{0.85}MA_{0.15}PbI₃ perovskite (curve 3). (*D*) Energy diagram showing the energy levels of all cell components as well as electron and hole transfer pathways.

scaffold and the penultimate process in the fabrication of a functional cell. In the concluding procedure, a perovskite precursor solution was allowed to seep through all three layers and crystalize between the NPs of the scaffold. Under illumination, a closed-circuit cell can now generate photocurrents and convert light to electrical energy. A cross section of the cell using a focused ion beam (FIB) is observed in Fig. 1B. The ordered threelayered structure on top of the FTO-coated glass can be depicted. As can be observed, the mpTiO₂ and mpZrO₂ layers are both ~1 µm thick, and the mpITO layer is ~3.5 µm. Absorbance measurements, shown in Fig. 1C, reflect the steps in the cell construction. The absorbance curve of the complete FTO/ mpTiO₂/mpZrO₂/mpITO scaffold extends slightly further into the visible range compared to the same configuration without mpITO (Fig. 1C, curves 1 and 2), indicating the scaffold's semitransparency. The absorbance of a completed cell with deposited FA_{0.85}MA_{0.15}PbI₃, which will later be used for the photovoltaic (PV) characterization, spans across the visible range (Fig. 1C, curve 3). When loaded with a wide-band gap perovskite, the scaffold allows most low-energy photons to go through (SI Ap*pendix*, Fig. S1A). The energy level alignment of the materials in this structure (17-20) is presented in Fig. 1D. This alignment, together with the electron transport qualities of the TiO₂, dictates an inhomogeneous average diffusion of free charge carriers. Exited electrons are efficiently and preferentially collected by the ETL, while the holes are readily collected at the massive perovskite-ITO interface.

The concluding step of the cell fabrication is the perovskite deposition onto the scaffold. Since the sintered mpITO cathode permits lateral conductivity, the evaporation of an extra metal contact is unnecessary. This renders the cells fully printable and easy to prepare. The cell architecture permits the use of various solvents as well as a plethora of perovskite compositions. The utilization of perovskites containing various iodide to bromide ratios demonstrates the possibilities offered by the scaffold (*SI Appendix*, Fig. S1 *B* and *C*). In this work we demonstrate the PV performance of mesoporous ITO-based PSCs (ITO-PSCs) using a mixed-cation perovskite composition of formamidinium and methylammonium lead iodide. Besides the optimal crystallization

conditions usually pursued in the synthesis of common PSCs, further criteria are essential for triple-oxide PSCs. The ample percolation of the perovskite solution through the nanometric cavities between the NPs of all layers is imperative. Additionally, to diminish the formation of empty voids in the network, following the crystallization of the perovskite and the evaporation of solvents, high-concentration precursor solutions are preferred. Several optimization experiments were carried out in order to attain high photovoltaic performance of the cells. SI Appendix, Table S1 presents comparisons between alternatively applied perovskite compositions, such as MA_{0.15}FA_{0.85}Pb(I_{0.85}Br_{0.15})₃, different paste formulations, and lead halide precursor concentrations. SI Appendix, Table S2 compares different dimethyl sulfoxide/ dimethylformamide (DMSO/DMF) ratios, used as a solvent in the lead halide precursor solutions, and their influence over the efficiency of the cells. Finally, SI Appendix, Table S3 exhibits the effect of dip orientation and duration on the overall performances. To this point, the ITO scaffold performances differ from other scaffolds mainly by their higher compatibility with the two-step deposition method.

The FA_{0.85}MA_{0.15}PbI₃ perovskite was deposited by a two-step deposition method using a high concentration of hot precursor solution. The two-step deposition method begins, as illustrated in *SI Appendix*, Fig. S2, with the administration of a metal halide solution on top of the substrate. A concentrated hot solution (2 M, 70 °C) of PbI₂ in an 85:15 ratio of DMF:DMSO was cast onto the mpITO layer in a nitrogen-filled glove box. By annealing the substrates at 100 °C for 30 min, a PbI₂ DMSO complex is formed (21). In the second step of the deposition process the cells were reacted with a solution of formamidinium iodide (FAI):methylamnonium iodide (MAI) (85:15) in isopropyl alcohol. Finally, annealing on a 100 °C hot plate for 30 min resulted in a black uniform perovskite. The top view scanning electron microscope (SEM) images (*SI Appendix*, Fig. S3) display a pinhole-free surface with no perovskite overlayer.

In order to further characterize the composition and structure of the cell and to assess the extent of the perovskite infiltration within it, an energy dispersive X-ray spectroscopy (EDS) analysis was performed on a cross-section of the cell. A FIB was used to



Fig. 2. Elemental mapping of a porous ITO perovskite solar cell cross-section using EDS. (A) Spatial scaffold element distribution across a mpITO PSC (as counts per second, CPS): indium (La1, blue, curve 1), zirconium (La1, maroon, curve 2), titanium (Ka1, green, curve 3), and tin (La1, yellow, curve 4). (B) Measurement path drawn on top of a SEM image of the specific analyzed area. (C) Spatial distribution of perovskite elements (as counts per second): lead (Ma1, black, curve I) and iodine (La1, red, curve II).

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excavate a cut through a completed cell, revealing its layered structure. The cross-section was scanned, and its elemental composition was analyzed and expressed as counts per second of the element-specific emission lines. Fig. 24 depicts the distribution of the main scaffold elements as a function of the sample depth. According to the EDS analysis, indium (curve 1) and tin (curve 4) atoms dominate the first 3 µm of the scan line. Deeper into the sample, signals of zirconium (curve 2), titanium (curve 3), and tin atoms appear as three separate well-defined bands. This elemental mapping matches the FTO/mpTiO₂/mpZrO₂/ mpITO structure and is in spatial agreement with the concomitant SEM image of the measurement area (Fig. 2B). The boundaries between the different layers in this image are evident. In the same measurement the distribution of the heavier perovskite elements is determined and is presented in a separate image for clarity (Fig. 2C). Detection of iodine and lead (curves I and II) is important here to identify the degree of percolation of the FA_{0.85}MA_{0.15}PbI₃ perovskite inside the mesoporous scaffold. Moreover, in this porous solar cell architecture the perovskite does not form a separate layer and is therefore virtually undetectable using SEM imagery, giving this method particular importance in the characterization of the embedded perovskite network.

Photovoltaic Performance of Triple-Oxide PSCs. Fig. 3*A* presents the current–voltage curve of the best-performing cell using $FA_{0.85}$ $MA_{0.15}PbI_3$ perovskite. This cell reached a power conversion efficiency (PCE) of 11.08% with open-circuit voltage (V_{oc}) of 0.988 V and current density (J_{sc}) of 17.55 mA/cm². An external quantum efficiency (EQE) measurement for a typical cell is presented in Fig. 3*B*. The integration of the EQE spectra gives a current density of 18.1 mA/cm², which is in very good agreement with J_{sc} obtained from the solar simulator. A J_{sc} histogram for the measured group of cells (30 cells) is presented in Fig. 3*C*. An average current density of 19.4 mA/cm² with SD of 1.8 mA/cm²

was received. These photocurrents exhibit the ability of the triple-oxide PSCs to successfully convert light energy into free charges and deliver them up to the contacts. These facts may be attributed to the enormous interface of both mpTiO₂ and mpITO with the perovskite network. Since ZrO₂ is an insulator, for every exciton formed, the electron and hole must have crossed accumulatively the whole mpZrO₂ layer. Hence, it is striking that the charges went through over 1 µm of thickness inside the labyrinth of the perovskite network between the ZrO_2 NPs with such efficiency. The Voc histogram presented in Fig. 3D shows an average Voc of 0.86 V with a SD of 0.1 V. Although these voltages are not comparable to state-of-the-art HTMcontaining devices using a similar perovskite composition, they constitute reasonable values for HTM-free cells. These types of cells possess structurally intrinsic lower Voc capabilities due to the extra overpotential necessary between the cathode and the perovskite. The fill factor (FF) histogram presented in Fig. 3E shows an average of 56.1% with a SD of 4.7%. Finally, the PCE histogram in Fig. 3F presents a rather narrow distribution of values, averaged at 9.37%, with a third of the cells exceeding 10% efficiency. The cells exhibit good reproducibility and a relatively low degree of hysteresis, as can be seen from the forward and reverse voltage scans shown in SI Appendix, Fig. S4. The active-area dependency of the cell performance is shown in SI Appendix, Fig. \$5. Though each ITO nanoparticle conducts electricity well, the mesostructured network of the particles is much less conductive. A significant part of the decrease can be attributed to the contact points between the particles, where they were fused together during the annealing process. This conductivity issue is less prominent in small active-area cells yet can cause charge buildup in the network with the increase of the active area (SI Appendix, Fig. S5A). Different locations on largescale screen-printed cells operate similarly to small cells (SI Appendix, Fig. S5B). Moreover, 5×5 cm cells show an average efficiency of 9.8%, where a typical JV curve can be observed in



Fig. 3. Photovoltaic characterization of ITO-PSCs with $FA_{0.85}MA_{0.15}PbI_3$ perovskite. (*A*) Current density vs. voltage (J–V) curve of the best-performing device under 100 mW/cm² air mass coefficient 1.5 global (AM1.5G) illumination, measured using a shadow mask dictating an active area of 0.09 cm². (*B*) EQE measurement of the best-performing cell (green) along with the integrated photocurrent (blue). (*C–F*) Measured value histograms of (*C*) short-circuit current density (J_{sc}), (*D*) open-circuit voltage (V_{oc}), (*F*) FF, and (*F*) PCE for 30 ITO-PSCs along with a normal distribution curve centered around the average value.

SI Appendix, Fig. S5*C*. Industrial manufacturing of the mpITO PSCs will have to include either multiple small-cell panels or the increase of mpITO network conductivity. Such an increase could be reached by performing the annealing at higher temperatures and for longer durations or by incorporating additives or other nanoparticle sizes or connecting a solid electrode network.

Stability and Renewability of Triple-Oxide PSCs. Stability measurements were carried out for a group of unencapsulated cells. These FA0.85MA0.15PbI3 perovskite cells were kept under ambient atmosphere conditions and repeatedly measured for a period of over 40 d, which corresponds to 1,000 h of stability measurement. The development of photovoltaic parameters over this time period is presented in Fig. 4*A*–*D*. It is noticeable that the average J_{sc} and V_{oc} values remain stable. As a result, the average PCE of the cells retains 96% of the cells' initial efficiencies. Other types of PSC configurations with similar perovskite compositions do not typically preserve their photovoltaic parameters as well when not encapsulated (22, 23). The decline in performance is usually attributed to moisture- and oxygen-related perovskite degradation. It is therefore conceivable that the stability of the triple-oxide PSCs stems from the perovskite's protected environment within the nanometric pores of the rigid scaffold. The renewability of ITO-PSCs originates from a number of structural qualities rooted in their unique design. The chemical and thermal stabilities of the scaffold enable the complete removal of an existing degraded perovskite network and the restoration of the scaffold's bare surface. All-component recycling of old PSCs has been demonstrated in the past (24, 25), showing the potential for recovery of materials, including the regeneration of perovskite from extracted solutions. However, it is notable that the major contributors to the cost of PSCs manufacturing, i.e., the anode, HTM, and the back contact, are not salvaged in these procedures. This fact, along with the unresolved issue of perovskite degradation on the years scale, induces a benefit in the ability to remove and replace only the

perovskite in a cell without compromising or removing other components. In this work, it was found that ITO-PSCs may be rinsed thoroughly with dimethylformamide for the removal of the perovskite from the scaffold. However, the ensuing application of new perovskite did not bring about a good restoration of the cell. Evidently, it was only once additional annealing of the rinsed scaffold (at 500 °C for 30 min) was performed that the cells could be restored simply by the application of new perovskite and reach their initial photovoltaic performances. Pictures of a device which was repeatedly rinsed and renewed using this procedure are shown in Fig. 4E. The photovoltaic parameters of eight cells were monitored throughout repeated restoration cycles and are summarized in Fig. 4F. Both restoration cycles yielded a slightly higher average J_{sc} and $V_{oc}\!,$ relative to the initial deposition, while the FF decreased by a few percent. X-Ray diffraction measurements of new and restored devices are compared in SI Appendix, Fig. S6. The spectrum of the latter appears to include more residues of PbI₂. These residues might be the result of incomplete rinsing during the restoration process and may be one of the reasons for the partial improvement in photovoltaic parameters, as they have been shown to be beneficial to cell performance (26). Additional contributions to the slight rise observed in J_{sc} and V_{oc} may be attributed to changes in the morphology and volume of the cavity network within the porous electrode caused by the initial perovskite crystallization process. Such changes might improve percolation and crystallization during the secondary deposition performed in the restoration cycle. Though not all influences are clear at the moment, the retention of the photovoltaic parameters is evident. The average PCE of the ITO-PSCs is fully restored after each cycle. For comparison, the same recycling procedure was conducted on carbon-based PSCs, and the results are shown in SI Appendix, Table S4. It can be seen that after one cycle only half of the treated cells displayed measurable photovoltaic performance, and after a second cycle, none were operational. Other attempts showed partial photovoltaic property restoration, using



Fig. 4. Mesoporous triple-oxide cell stability and restoration. (A–D) Trends in normalized values of (A) J_{scr} (B) V_{ocr} (C) FF, and (D) PCE for unencapsulated FA_{0.85}MA_{0.15}Pbl₃ cells stored under ambient atmosphere over a period of 42 d. The error bars represent the SD from the normalized value averaged over all measured cells. (E) Photographic account of two cell restoration cycles. DMF is used to wash away old perovskite, and a new one is deposited. (F) Changes in normalized values of J_{scr} , V_{ocr} , FF, and PCE over two restoration cycles. The error bars represent the SD from the normalized value averaged over all measured cells.

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comparable methods but a different cell framework (27). The renewability of the ITO-PSC scaffold, on the other hand, is a prominent feature of this cell architecture and can be used to construct fully recyclable and sustainable PSC modules.

Investigation of the environmental impact, in terms of life cycle assessment (LCA), provides insights into the different environmental, ecological, and health effects of a product's mass production. LCA brings into account all of the materials and energy consumed, starting from raw materials and ending with their ultimate disposal. LCA research conducted on perovskite solar panels has previously highlighted their relatively low level of environmentally harmful effects as a benefit compared to various other solar technologies (28). The results showed that the most significant portion of energy consumption during the fabrication was attributed to the usage of FTO- or ITO-coated glass and evaporated gold electrodes. These two materials are also responsible for most of the product's various environmental impacts, such as acidification potential, eutrophication potential, and others, according to the CML (Institute of Environmental Sciences at the University of Leiden, the Netherlands) method. In the current research the mpITO scaffold is recyclable and renders the gold electrode unnecessary. To further inquire about the advantages of the presented mpITO scaffold, it was necessary to confirm the environmental impacts of the renewal process. SI Appendix, Table S5 details the estimated energy consumption for the restoration processes of 1 m² of ITO-PSCs. The main power-consuming process is the sintering of the recovered scaffold. Additionally, SI Appendix, Table S6 contains an inventory of the materials consumed in the recovery processes. It includes the removal of the former perovskite layer, redeposition materials, and the disposal of all materials involved in these processes. Further reusage of the perovskite, through reconstitution of precursor materials from the waste, should minimize the environmental impact solely to energy consumption. In terms of energy payback time (EPBT), the recovery process allows values of 0.45 to 0.54 y if installed, for example, in parts of the Israeli Negev desert, where the average solar radiation can reach 2,365 kWh/m² per year (29). This calculation assumes 10% PCE and 80% active area. The life cycle impact assessment of the recovery process is laid out in SI Appendix, Tables S7 A and B. The assessment indicates an Eco-indicator 99 total of 0.89 ± 0.04 points, which is composed of an Eco-indicator 99 - ecosystem quality of \sim 0.44, a human health factor of 0.22 to 0.25, and a resources factor of 0.20 to 0.23. MAI evidently contributes the most to all three factors and accounts for almost half of the accumulative energy consumption. Therefore, its recovery from the DMF solution can substantially reduce both the Ecoindicator 99 and the EPBT results. Nonetheless, remarkably low Eco-indicator 99 results express an enduring low environmental impact and speak to the virtue of a full restoration of the device via perovskite layer reinstatement and the reuse of the robust scaffold.

Charge Extraction and Intensity-Modulated Photovoltage Spectroscopy.

To further investigate the physical properties of this solar cell type, charge extraction (CE) and intensity-modulated photovoltage spectroscopy (IMVS) measurements were carried out. The CE measurement is conducted by illuminating the cell for 5 s under open-circuit conditions then switching off the light and allowing the internal charges to decay for a varying period of time (delay time). Subsequently, the cell is short-circuited, and the remaining charge is extracted and quantified. Fig. 5A plots the extracted charge as a function of the delay time before a short circuit was induced for both an ITO-PSC (curve 1) and a carbon cathode PSC (curve 2), which bears resemblance in structure to the ITO-PSC and was prepared using the same perovskite composition. The measurements show a faster decay of charges in the ITO cell compared with the carbon cell. The decay of charges in the cell reflects the recombination of free charge carriers generated by the initial illumination. Since the recombination lifetime within the perovskite is on the order of nanoseconds (30), it is widely thought that the observed retention of charges over several seconds represents the existence of trap states on the perovskite–scaffold interface (31, 32). These states enable prolonged segregation of the charge carriers. The amount of charge extracted in the CE measurements is therefore assumed to be indicative of the presence of traps at the cell's interfaces.

IMVS was used to study the recombination behavior in the ITO-PSCs. For comparison, carbon cathode PSCs, prepared similarly and containing the same perovskite composition, were measured with IMVS as well. In this technique the cell was illuminated by white light with modulated pulse frequencies ranging between 1 and 10^5 Hz. When measuring the transfer function, the impedance of the cell can be assessed, and an equivalent circuit can be assigned to it. This basic IMVS measurement was repeated at different light intensities ranging from 0.1 to 0.7 sun. When plotting the impedance in the complex plane, two semicircles were observed (*SI Appendix*, Fig. S7) for each light intensity. One semicircle appears at high frequencies of 10^4 to 10^5 Hz, and the other appears at lower frequencies of around 10^2 Hz. By identifying the frequency at the minimum of



Fig. 5. Charge extraction and IMVS measurements. (A) Values of extracted charge as a function of delay time after illumination for an ITO-PSC with $FA_{0.85}MA_{0.15}Pbl_3$ perovskite (curve 1) and a typical porous carbon PSC with the same perovskite composition (curve 2). (B) The first observed lifetime as a function of light intensity, calculated from IMVS measurements of a $FA_{0.85}MA_{0.15}Pbl_3$ ITO-PSC (curve 1) and a carbon PSC with the same perovskite (curve 2). Exponential decay fittings appear as dashed lines.

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each semicircle, one can extract the characteristic lifetime it represents. The first set of semicircles, found at high frequencies $(10^4 \text{ to } 10^5 \text{ Hz})$, corresponds to lifetimes on the order of 10^{-3} to 10^{-2} ms, whereas the second set, observed at lower frequencies (10^2 Hz) , corresponds to lifetimes on the order of 0.1 to 1 ms. Both lifetimes show a negative exponential dependence on light intensity. It is generally believed that this type of dependency originates from the direct influence of light intensity on the charge carrier density in the perovskite (33). The higher the carrier density is, the higher the probability of oppositely charged carriers encountering each other and recombining is, thereby decreasing their average lifetime. The longer of the two observed lifetimes (SI Appendix, Fig. S8) is commonly assigned to the behavior of charges in the TiO2, which possesses intrinsically slower recombination rates (34). The shorter lifetime, on the other hand, is usually attributed to charge recombination in the perovskite itself. Higher carrier lifetimes are revealed by IMVS measurements of the more conventional PSC structures (33). In Fig. 5B, a comparison of the ITO-PSCs (curve 1) and the carbon PSCs (curve 2) reveals that though the ITO-PSCs possess slightly shorter lifetimes, they are well within the same regime as the carbon cells. This finding suggests that the structural differences between these two cell types have no significant effect on recombination lifetimes in the perovskite, as is expected considering the use of the same perovskite composition.

Conclusions

In conclusion, a configuration for perovskite solar cells was presented. These mesostructured triple-oxide perovskite solar cells revealed high stability for unencapsulated cells. These properties are derived from the unique all-NP scaffold and the interlaced perovskite network which is crystalized within its cavities. Other than being fully printable, the cells were proven to be entirely renewable. Removing the perovskite allowed the application of a new one and the retrieval of the initial photovoltaic performances. Since these cells permit direct solution perovskite deposition as a final step, we consider this architecture to be a general platform for the fabrication of solar cells and various optoelectronic devices. Renewal of the photoactive materials is one step forward in the endeavor for sustainable green energy production.

Methods

Materials and Solvents. Hellmanex III detergent, Ti diisopropoxide bis(acetylacetonate) (75% weight [wt.], in isopropanol), ethyl cellulose (46070 and 46080), terpineol, indium tin oxide (nanopowder <50 nm particle size), Pbl₂ (99%), *N*,*N*-dimethylformamide (anhydrous 99.8%), and isopropyl alcohol (anhydrous 99.5%) were purchased from Sigma-Aldrich. MAI, FAI, and titania paste (90 T) were purchased from GreatCell Solar. Titanium (IV) chloride was purchased from Wako. Ethanol absolute (99.5%) and extra dry dimethyl sulfoxide (99.7%) were purchased from Acros. Zr-Nanoxide (46411) was purchased from Solaronix. Carbon paste was purchased from Feiming. All fabrication precursors were performed in a nitrogen-filled glove box, and the materials were used as received.

Preparation of ITO Nanoparticle Paste. A solution of ethyl cellulose solution (10% wt.) was prepared by dissolving equal weights of two ethyl celluloses of different viscosities (Sigma 46070 and 46080) in ethanol and was magnetically stirred overnight; 1.2 g of ITO nanopowder were processed repeatedly using a mortar and pestle. First, five 1 min cycles of grinding were coupled with the addition of 200 μ L triple distilled water every cycle; then, fifteen 1 min grinding cycles ensued with the addition of 200 μ L triple distilled water every cycle; then, fifteen 1 min grinding sequence was complete, the formed cement was diluted in 20 mL of ethanol, and 1.95 g of terpineol were added. The mixture was then dispersed using a magnetic stirrer and a sonic horn (50 half-second pulses). Next, 2.88 g of the cellulose solution were added and mixed similarly using a magnetic stirrer and sonic horn. The mixture was finally stirred on a hot plate at 50 °C for 24 h until the ethanol was evaporated completely.

mpITO Scaffold Slide Preparation. The slides were prepared similarly to a previously described procedure (35). In brief, FTO-coated slides were etched to segregate anodal and cathodal areas. The slides were rinsed and put in an ultrasonic bath (three cycles of 15 min: in soap, in Hellmanex detergent [1% in water], and in pure water). The substrates then underwent argon plasma treatment for 10 min. For a blocking layer treatment, the substrates were spin coated by a 13.3% titanium diisopropoxide bis(acetylacetonate) solution (5,000 rpm, 30 s in ethanol), then annealed on top of a hot plate (30 min, 450 °C).

Later, the slides were treated by a TiCl₄ solution (1.6 mL TiCl₄ in 150 mL water) and put in an oven (70 °C, 30 min). Promptly, the slides were annealed on a hot plate (450 °C, 30 min). Subsequent to cooling to room temperature, TiO₂ paste was screen printed onto the slides but not the exposed FTO area, using a 120 mesh screen, and sintered at 500 °C for 30 min on a hot plate. Later on, the aforementioned TiCl₄ treatment was repeated and was followed by the screen printing of ZrO₂ paste using a 120 mesh screen which was then sintered (500 °C, 30 min). The ITO paste was finally screen printed using a 45 mesh polymer screen and sintered at 600 °C for 90 min. To prepare carbon-based substrates, all fabrication steps were conducted in the same manner as for ITO cells, but instead of the ITO paste, a carbon paste was printed and sintered at 500 °C for 30 min.

Perovskite Solution Preparation and FA_{0.85}**MA**_{0.15}**PbI**₃ **Two-Step Deposition.** The mpITO scaffolds were inserted into an inert atmosphere glove box and heated on a hot plate (200 °C, 30 min). Later, PbI₂ solution (2 M, 0.5 mL) in a 85:15 DMF:DMSO mixture was prepared; 2 μ L of the solution were cast onto the mpITO substrate's active area and annealed at 100 °C for 30 min. The substrates were then immersed in a 0.06 M solution of FAI:MAI at a ratio of 85:15 in isopropyl alcohol for 20 min and then dipped in clean isopropyl alcohol for 5 s. Subsequently, the cells were annealed on a hot plate (70 °C) for 30 min to finalize the preparation process.

Cell Cleaning and Restoration. The perovskite crystals embedded in the substrate were dissolved and washed away by dripping DMF on the cell (5 mL). The cleaned cells were then heated to 500 °C for 30 min. The subsequent deposition process was carried out following the same procedure as described above.

SEM, FIB, and EDS. To obtain a high-quality cross-section of the cell for SEM imagery and EDS analysis, a sample was placed inside a FEI Helios NanoLab 460F1 and excavated using a focused gallium ion beam to expose the layered structure. The layered stack was imaged and measured, and a slab was retrieved and placed on a separate holder to enable a 90° EDS line scan. The EDS scan was conducted using electron beam energies between 5 and 30 kV in order to recognize the desired elements.

Absorbance and Transmittance. The absorbance measurements of substrates and cells were conducted using a Varian Cary 5000 ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer equipped with a Varian DRA 2500 diffuse reflectance accessory (integrating sphere). Transmittance measurements were carried out with a Jasco V670 spectrophotometer.

Work Function. To determine the work function (WF) of a porous ITO film, a SKP5050-SPS040 model Kelvin probe system was used. The contact potential difference (CPD) between the sample and the vibrating tip was measured with the sample inside a Faraday cage under an ambient air environment. Before the measurement, the sample and tip were allowed to stabilize for about 30 min. The final WF value of the sample was calculated according to $WF_{sample} = WF_{tip} + CPD_{sample}$ with the WF function of the tip being obtained using a gold-coated calibration stage.

Hall Effect and Conductivity. Hall effect measurements and sheet resistivity calculations were conducted using a model 4804 AC/DC Hall effect measurement system, manufactured by Lake Shore Cryotronics.

Photovoltaic Characterization. Current–voltage measurements were performed using a solar simulator system (Oriel I–V test station, Sol3A simulator with a 450 W Xe lamp and output power of air mass coefficient 1.5 global sunlight). J–V curves were obtained by applying a varying external bias on the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. For standard measurements a forward voltage scan was conducted from 1 to –0.1 V with voltage step and dwell times of 10 mV and 40 ms, respectively. For hysteresis measurements a reverse voltage scan was conducted from –0.1 to 1 V. Photovoltaic performance was

measured using an opaque mask with an aperture area of 0.085 cm² (measured using an optical caliper). Cells were measured at least 24 h after fabrication, and J–V curves were measured repeatedly until stabilization of the maximum power point. For PV performance vs. active-area measurements, three mask apertures were used: 0.09, 0.13, and 0.19 cm².

EQE measurements were obtained using a custom-made (by PV measurements) incident photon to current efficiency device containing a tungsten lamp for bias and a xenon lamp with a monochromator for wavelength scan. Measurements were conducted under no-bias light or external voltage, in AC mode, using a light chopper set at 30 Hz. A standard silicon photodiode was used to calibrate the device.

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CE and **IMVS.** CE and IMVS measurements were carried out by an Autolab potentiostat galvanostat instrument through a previously published procedure (35).

Data Availability. All study data are included in the article and SI Appendix.

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