Free-standing nanopaper electrode for all-printed super-flexible perovskite solar cells

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Abstract

The development of all-printed, flexible solar cells of high efficiency and ultra-low weight will offer advancements for new market entrants. Herein, we report the design and fabrication of all-printed in ambient air, super-flexible perovskite solar cells with approaching 20% power conversion efficiency and extremely low weight of 5.1 g m⁻² leading to an unprecedented power-to-weight ratio of 38,470 W Kg⁻¹. This performance advance was achieved through the design of a highly transparent and conducting nanopaper used as a free-standing bottom electrode (FSBE). The FSBE consisted of cellulose nanocrystals grafted with semi-metallic super-reduced polyoxometalate clusters that enabled high conductivities up to 18 S cm⁻¹ combined with transparency >96%. It also acted as a conformal barrier preventing performance loss upon heating at 95 oC under continuous illumination in inert environment; and strong resistance to decomposition when immersed in a mild citric acid water solution for 100 days, which we further exploit to demonstrate full device recyclability. The inherent flexibility of cellulose nanocrystals enabled remarkable flexibility of these cells under 2,000 repeated bending and folding cycles and mechanical strength upon extensive strain up to 20%. Notably, the nanopaper remained unaffected for strains up to 60%. These findings open the door for efficient and lightweight solar cells with a low environmental impact.

Main Text

Thin and lightweight solar cells of high specific power that are flexible and elastic under tensile strain are appealing for emerging applications in aerospace, unmanned aerial vehicles and integration in automobiles, buildings, textiles and moving parts of machinery¹. Key elements that will enable the flexible solar cell technology to further evolve are the development of low-cost and abundant materials for the device substrate, electrodes and functional layers combined with the capability to be printed using high-yield low-cost methods. Promising candidates are the emerging photovoltaic technologies based-on solution-processed semiconductors, such as organics², colloidal quantum dots³ and organic-inorganic halide perovskites⁴. Particularly, perovskite solar cells (PSCs) have already reached commercially viable power conversion efficiencies (PCEs) up to 25.2%⁵⁻⁸ for rigid devices fabricated on glass substrates and up to 20.7% for flexible ones fabricated on plastics⁹⁻¹³. This progress was realized by tailoring the composition and dimensionality of the perovskite absorber, advancements related to low-temperature deposition methods to improve the perovskite layer's properties, and interface materials to improve the energy level alignment¹⁴⁻²⁰.

However, the majority of the existing solar cells, including perovskite ones, are fabricated either on glass or on plastic substrates coated with indium tin oxide (ITO) or fluorinated tin oxide. These substrates increase the device thickness and weight (especially glass) and are unsuitable when considering fully solution printing capability of solar cells²¹⁻²³. More importantly, the conductive ITO layer (a commonly utilized electrode material for a vast variety of optoelectronic devices), is both expensive and mechanically fragile. Low-cost, Earth-abundant, and easily recyclable materials for substrates and

electrodes of solar cells are desired to overcome this bottleneck. Efforts to replace ITO with alternative electrode materials include graphene¹⁴, single wall carbon nanotubes²⁴, doped-metal oxides²⁵, silver nanowire (Ag NW) networks^{26,27} and conducting poly(3,4-ethylenedioxythiophene) polystyrene sulfonate^{23,28}. To avoid the use of glass and plastics, sustainable paper substrates derived from cellulosic pulps have been recently explored due to their abundance, environmental friendly properties, renewability and sufficient mechanical tolerance²⁹. However, these papers are commonly made of microcrystals/microfibers, which scatter significant portion of the incident light and, hence reduce their transparency³⁰. To increase transparency, nanocellulose papers have been recently explored, but still require the additional deposition of conductive electrode materials – thus increasing the complexity of device fabrication³¹⁻³⁶. Development of sustainable materials combining both high transparency and adequate conductivity to serve as FSBs for solar cell application and beyond will offer advancements in many fields of renewable energy harvesting devices.

In this study, we report that super-reduction of polyoxometalate (POM) clusters grafted onto a cellulose nanocrystalline (CNC) matrix can create a highly conductive and transparent nanopaper, which serves as a free-standing device bottom electrode for the fabrication of substrate-free PSCs printed in the air *via* a facile solution shearing method. The devices exhibited a PCE of 19.89% combined with a total thickness of only 0.8 μm , a weight of 5.1 g m^{-2} and a power-to-weight ratio of 38,470 W Kg^{-1} , which render it the thinnest, lightest, and yet high PCE solar cell made to date^{1,28}. The composite nanopaper acted as a conformal coating that enabled practically unchanged device efficiency upon heating at 95°C under continuous illumination in inert environment. It also protected the device layer from decomposition when immersed in a mild citric acid water solution for 100 days and enabled superior mechanical robustness upon multiple bending and folding cycles and upon the application of strain.

Development of FSB

Cellulose paper substrates are commonly made from fibers having large diameters up to 20 μm , which backscatter a significant portion of the incident light and are either optically opaque or semitransparent. Furthermore, the large size and the high packing density of these fibers hinders their use as a reversibly deformable paper substrate. To overcome the inherent limitations of microcrystalline cellulose papers, nanopapers made from cellulose nanofibers or nanocrystals (NCs) were recently developed³⁷. Nonetheless, despite being sufficiently transparent, these nanopapers are highly-insulating, thus requiring additional electrode materials prior to the device fabrication. Instead of depositing additional electrode, which makes the device fabrication more complex, our work has focused on endowing the nanopaper with high conductivity without compromising its transparency. To this end, we explored the suitability of a well-known family of solution-processed molecular oxides namely polyoxometalate (POM) clusters. We have previously demonstrated that nearly metallic conductivities can be achieved by highly reduced POM clusters of either Keggin or Wells-Dawson type³⁸. Here, we designed and developed a highly transparent and conducting nanopaper consisted of super-reduced POM clusters grafted onto cellulosic NCs of small size. The cellulose NCs were synthesized *via* a multistep procedure initiated by acid hydrolysis of the

cellulosic pulp as explained in Methods. In brief, a concentrated sulfuric acid solution was first added in the pulp causing the dissolution of the amorphous regions of the cellulose molecular chains whereas the highly crystalline regions remained intact. The molecular diagram in Fig. 1a depicts two of the crystalline cellulose chains comprising the NCs, which formed through multiple hydrogen bond interactions between these chains. The procedure requires repeatable purification steps (Supplementary Fig. 1); it results in the formation of a white powder consisted of the needle-like NCs with diameters of 30-50 nm and lengths of 150-350 nm (Fig. 1b). Next, these NCs were mixed with urea (NH_2CONH_2), a well-known thermal stabilizer for cellulose and reducing agent for POMs, and ammonium metatungstate hydrate $((\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot x\text{H}_2\text{O})$ POM nanoparticles with an average size of 1 nm (Fig. 1c) and dissolved in a mixture of deionized (DI) water, sodium hydroxide (NaOH) and hydrochloric acid (HCl). The specific POM was selected among a large variety of POM clusters tested, because it was capable of undergone a very high degree of reduction which was retained for more than a year under storage. It was also very stable to heating up to 150 °C and 1.5 AM simulated light exposure for many weeks. After extensive optimization of the concentration of the constituents, the resultant ink was printed on a solid support *via* a solution shearing method; a simple, fast and a low-cost procedure that is suitable for up-scaling. In the printed nanopaper the cellulosic NCs exhibited a moderate degree of orientation with only few POM aggregates between them (Supplementary Fig. 2). Transmission electron microscopy (TEM, Fig. 1d) and X-ray diffraction (XRD, Supplementary Fig. 3) indicated that POM clusters were grafted onto the cellulose NCs. Remarkably, the printed nanopaper was very conductive for a wide range of printing conditions and resultant thicknesses (Fig. 1e and Supplementary Table 1). The conductivity originated from the high degree of reduction, termed as super-reduction, of POM clusters in the cellulose:urea:POM. To unravel the origin of super reduction of POMs, we performed an extended study of cellulose:POM and urea:POM composites (Supplementary Note 1 includes the detailed discussion about the urea-induced super-reduction of POM). X-ray photoelectron (XPS) and UV-Vis absorption (Supplementary Fig. 4), Fourier transform infrared (FTIR) (Supplementary Fig. 5), ultra-violet photoelectron (UPS, Supplementary Fig. 6) spectroscopy measurements taken in urea:POM composites indicated electron transfer from urea molecules to POM^{38,39}, as illustrated in Fig. 1f. Notably, there was no evidence for POM reduction in cellulose when urea molecules were not present. Urea bears two lone pairs per molecule that lying above and below the molecular plane and are hence prone to transfer to a low lying LUMO molecule like POM⁴⁰. XPS results revealed that about 12 excess electrons were up taken by each cluster, which resulted in a large negative charge of -18 per cluster. This negative charge is partially compensated by the positive charge of amines in urea molecules that were coordinated and anchored in the outer shell of POMs (Supplementary Fig. 5). The sr-POM clusters were subsequently uniformly anchored onto the cellulose NCs through the formation of extended hydrogen bond interactions (Fig. 1g and Supplementary Fig. 7). This prohibited the formation of large aggregates and increased the visible transparency (Supplementary Fig. 4d). Regarding the electronic structure of srPOMs, UPS measurements revealed that their valence band maximum (VBM) is extended up to the Fermi level (Supplementary Note 2 and Supplementary Fig. 6). This VBM has mainly O2p character, while the conduction band minimum (CBM) is composed of W5d atomic orbitals with the 5d_{xy} to have the lower energy⁴⁰⁻⁴². According to the electronic structure proposed

by Nishimoto et al. for super-reduced α -Keggin POMs⁴⁰, we consider our srPOM clusters as the total of four identical substructures consisted of metal triangle features originating from the formation of tungsten-tungsten bonds upon the uptake of excess electrons. The three additional electrons per metal triangle substructure are placed in $5d_{xy}$ orbitals with e and a_1 in symmetry as shown in frontier molecular orbital (MO) diagram of the substructure (Fig. 1h, middle). With a total of 12 excess electrons per cluster, half of the metals are in the 4+ state. In order to preserve their skeleton, the super-reduced structure squeezes out oxygen bridging two neighboring W atoms, which form covalent metal bonds. The decreased metal-metal distance in the metal triangular configuration enhances the overlap of these orbitals and lowers their relative energies. Once the substructures are connected into srPOM, the four a_1 and eight e frontier MOs containing the excess electrons split into groups of one a_1 and three t_2 (for a_1) and two e, three t_1 and three t_2 (for e) MOs, respectively (Fig. 1h, right). The 12 excess electrons fill the MOs with lower energies (t_2 , a_1 and e in symmetry), which are located near the Fermi level. As a result, the srPOMs exhibit semi-metallic behavior and endows the resultant nanopaper with conductivity values up to 18 S cm^{-1} . The transparency of the nanopaper is also very high for a wide range of thicknesses (Fig. ij and Supplementary Table 2) reaching 96.4% transmittance (at 546 nm). This is the synergistic result of the high transparency within the visible spectrum of srPOM clusters when they are uniformly grafted onto cellulose NCs (Supplementary Fig. 3). However, the high transparency mainly stems from the reduced light backscattering efficiency caused by the small NCs of 30-50 nm in diameter⁴³; the light backscattering efficiency is inversely proportional to the size of the NC. As a result, the light propagation in the forward direction is significantly strengthened. Notably, a highly transparent (94.5 % at 550 nm) cellulose nanopaper has been recently reported through in situ photo-polymerization of the conductive polymerizable deep eutectic solvent (PDES) monomer⁴⁴, albeit with a very low conductivity of 0.0013 S cm^{-1} .

Solar cell fabrication and performance

Among the low-cost thin film printing techniques, solution shearing has the advantage of yielding minimum waste of precursor solution (<10% of the amount required for spin-coating) and allowing for direct thin film crystallization near the edge of the meniscus⁴⁵. We applied the solution shearing printing method in the fabrication of all device layers including the nanopaper which served as a free-standing device bottom electrode (Fig. 2a). Moreover, we combined this method with a vacuum flash-assisted (VASP) processing for the deposition of the perovskite film⁴⁶. The combination of solution shearing with VASP enabled the formation of high-quality perovskite layers, having large grains on the order of micrometer (Supplementary Fig. 8), and superior optoelectronic properties (Supplementary Fig. 9). The PSC architecture was: CNC (160 nm)/tin oxide (SnO_2 , 40 nm)/phenyl-C61-butyric acid methyl ester (PCBM, 10 nm)/perovskite (330 nm)/Spiro-OMeTAD (70 nm)/Ag NWS (160 nm) (Fig. 2b) having a total thickness of 770 nm (substrate included). The SnO_2 /PCBM bilayer and Spiro-MeOTAD were used as the electron and hole transport layers (ETLs/HTLs), respectively. The light absorber was a quadruple cation RbCsMAFA (Rb:CsMAFA 10:90) perovskite having the triple cation perovskite chemical structure of

$\text{Cs}_{0.5}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.5}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$, where Rb is rubidium, Cs is caesium, MA and FA are methylammonium and formamidinium, respectively⁴⁷. Fig. 2c depicts a representative cross-section scanning electron microscopy (SEM) image of the complete PSC device. High-angle annular dark-field (HAADF) image and energy dispersive X-ray spectroscopy (EDS) mapping in scanning tunneling electron microscope (STEM) mode confirmed the homogeneous distribution of Rb and Cs elements in the perovskite layer obtained through printing (Fig. 2d). Notably, for the top cathode we adopted a non-aqueous processing procedure for the deposition of an orthogonal array of Ag NW ink (see Supplementary Note 3 for more details). Ag NWs were embedded into a cellulose matrix instead of the commonly used, hydroscopic PEDOT:PSS. Our process enabled the fabrication of high-elastic Ag NW orthogonal arrays (Supplementary Fig. 10), without affecting the quality of the perovskite layer underneath.

Figure 3a presents the current density-voltage (J-V) characteristics of the 0.25 cm^2 champion device fabricated on nanopaper after an extensive optimization study (Supplementary Figs. 11 and 12). The device exhibited high open circuit voltage (V_{OC}), short-circuit current density (J_{SC}) and fill factor (FF) that gave rise to a maximum PCE of 19.72% in the forward scan (FS) and 19.89% in the reverse scan (RS) (Table 1). Remarkably, this nanopaper-based PSC exhibited negligible hysteresis, high external quantum efficiency (EQE) above 90% in the visible, a stable V_{OC} over time, and a mean PCE value of 19.32% (Supplementary Fig. 13). Due to the high optical transparency of both the free-standing bottom electrode and the top electrode, it also exhibited a small semi-transparency (i.e. an average transmittance (AVT) of 11.86%), which could further improved, albeit on the expense of the device efficiency (Supplementary Fig. 14). Interestingly, a larger area ($1\times 1\text{ cm}^2$) device delivered a PCE of 17.35% and a stabilized PCE of 17.16% (Fig. 3b and Supplementary Table 3). This also originated from the successful combination of solution shearing and VASP methods for the printing of perovskite absorber as indicated by the high efficiencies obtained in various PSCs based on either ITO/glass or ITO/PET substrates (Supplementary Fig. 15 and Supplementary Tables 4-6). Notably, a PCE of 22.08% achieved in the rigid device (ITO/glass) represents a record for PSCs processed *via* solution shearing and is among the highest efficiencies reported to date for printed PSCs⁴⁵. The nanopaper-based device represents the best performing flexible perovskite solar cell, including devices fabricated on plastic/ITO substrates (Supplementary Tables 7 and 8). Besides the high efficiency, the device is extremely thin (i.e., $0.8\text{ }\mu\text{m}$ thick), and lightweight (5 g m^{-2}), leading to an unprecedented power-to-weight ratio of $38,470\text{ W Kg}^{-1}$ for the champion cell ($38,060\text{ W Kg}^{-1}$ at MPP). Clearly, the nanopaper-based PSCs offer a great advantage for lightweight power generation.

Stability and recyclability

During operation, solar cells are exposed to sunlight. As a result, they are constantly heated due to the absorption of thermal radiation. It has been reported that solar modules operating in hot climate may reach temperatures of over $65\text{ }^{\circ}\text{C}$ ⁴⁸. Moreover, device fabrication may require high temperature post perovskite deposition processes, such as annealing of charge transport overlayer and device encapsulation. To track the effect of continuous heating, we measured the variation of PCE of the

encapsulated cells that were heated at 95°C for 1,000 hours under continuous 1 sun illumination at maximum power point (MPP) tracking in a nitrogen atmosphere (Fig. 3c). Remarkably, during light exposure at 95°C, the device retained 99% of its initial performance. The high thermal stability of our PSCs is attributed to the superior properties of the perovskite absorber and the nanopaper. With our solution shearing printing combined with VASP, we were able to deposit highly-oriented perovskite layers having large (on the order of micrometer in size) grains, thus reducing the deleterious effect of grain boundary defects. This was verified by the high stability obtained in several types of rigid and flexible PSCs tested upon continuous illumination in nitrogen (Supplementary Fig. 15) or in ambient air (Supplementary Fig. 16). However, the stability of the nanopaper-based device was superior compared to others, which indicates that CNC layer has also a contribution. To explain such remarkable stability of CNC-based devices we can consider the close matching of the thermal expansion coefficients of perovskite ($1.5 \times 10^{-4} \text{ K}^{-1}$) and the cellulosic substrate ($1.3 \times 10^{-4} \text{ K}^{-1}$). This results in minimum thermally-induced device stress upon heating. Moreover, the addition of urea in cellulose matrix has been previously shown to highly expand the thermal stability of the resultant paper⁴⁹. This is because carboxylic acids acting as hydrolysis-induced degradation sites in cellulose are partially neutralized by forming a stable salt with the respective amines. Moreover, the addition of urea and POM in the cellulosic matrix resulted in a more hydrophobic nanopaper in comparison to pristine cellulose sample (Supplementary Fig. 17), indicating that a reduced water content within the composite nanopaper. We note that a similar concept of amine molecules addition, termed as the “alkaline reserve in cellulose conservation science”, is applied by librarians and archivists to preserve historic acidified papers and books in the best possible manner.

An additional advantage of renewable energy devices is the ability to be fully-recyclable using low-cost methods in order to have minimal effect on environmental pollution. Glass and metal electrodes, however, present significant constraints for the recyclability of solar cells even when they are fabricated from solution-processed absorbers and interlayers. Perovskite layers have been recently shown to be fully recyclable using appropriate solvent combination⁵⁰. However, the use of glass and metals adds significant drawbacks to make the existing PSCs environmentally-friendly. Our nanopaper-based PSCs are glass and ITO-free and undergo full degradation when continuously exposed to a mild citric acid (5% wt) water solution heated at >155°C (see also Supplementary Note 4 for details). Notably, the device exhibited a remarkable stability to decomposition when continuously immersed for 100 days (Fig. 3d). The device recyclability was only initiated by heating at 155 °C and above, where the hydrolysis of cellulosic material -probably in both electrodes- is initiated according to a scheme presented to Supplementary Fig. 18. The degradation reaction results in the formation of a furan-based bio-oil. After the cellulosic material has been transformed and removed, the citric acid etches and dissolves the SnO_2/PCBM layer, whereas water decomposes the perovskite absorber. Notably, this experiment not only demonstrates the full recyclability of our device in a mild acidic solution but it also proves its high resistance to moisture-induced degradation for 100 days before the application of heat. This could be a consequence of suppressed carboxylic acid initiated hydrolysis of cellulose upon urea amino groups' coordination as explained above.

Flexibility and stretchability studies

For practical applications, the mechanical durability of PSCs under bending, folding and application of strain (Supplementary Fig. 19) is of significant importance. To evaluate the flexibility of nanopaper-based PSCs, we subjected the devices to bending (Fig. 4a) and folding (Fig. 4b) tests. In the first case, tensile strain is applied to the perovskite absorber whereas in the second case the absorber is subjected to compressive strain. Our device displays excellent mechanical bending/folding stability even after a 2,000-cycle bending/folding test at curvature radii of 2.0, 1.0 and 0.5 mm. Negligible changes are observed in all device performance characteristics (J_{SC} , V_{OC} and FF) upon bending and release for 2000 cycles. Similar results were obtained for the folding stability tests where the perovskite absorber is subjected to compressive instead of tensile strain. The small decline in efficiency after 2000 folding cycles is mainly due to a loss in V_{OC} . On the contrary, a small increase in the device FF after the repeated folding tests could be due to an increase in mobility in the perovskite layer due to the decrease in the inter-lattice distance during folding⁵¹. This extraordinary bending and folding stability of our flexible PSCs built on nanopaper (Fig. 4c), can be explained on the basis that cellulose nanocrystals with such small size can be reversibly transform during each cycle of mechanical deformation. This is a great advantage of our nanopaper relative to the regular paper commonly used (which consists of large cellulose fibers of the order of 20 μm) as well as the plastic substrates. The small size of the building blocks of our nanopaper results in the formation of a nanoporous network in each layer that adsorbs strain more easily compared to rigid substrates. Besides being flexible, our device was also subjected to the application of tensile strain and found quite durable for strains up to 20% (Fig. 4d and Supplementary Fig. 20). A significant failure caused by crack formation and propagation was initiated first in the perovskite layer only when the strains were above 20% (Supplementary Fig. 21). Cracks in the nanopaper substrate appeared for strains over 60%, which indicates that our FSBE is capable of very high mechanical strength. However, upon keeping the applying strain below 20% the device performance was quite stable for multiple cycles of strain and release (Figs 4 e,f), indicating that fabrication of a solar cell on a conformal nanopaper composed of small nanocrystals is very promising for emerging applications such as wearable electronics.

In this study, we present a choice of materials and device fabrication methods that allowed the development of highly stable all-printable, fully recyclable perovskite solar cells with a record figure of merits including being lightweight and ultra-thin, reaching very high efficiency and record power-to-weight, and demonstrating enhanced thermal and mechanical durability. These cells were fabricated on highly transparent and conducting nanopapers composed of cellulose nanocrystals grafted with super-reduced semi-metallic polyoxometallate clusters. The nanopaper served as the device free-standing bottom electrode. The application of a non-aqueous solution processed cellulose:Ag NW composite top electrode, synergistically contributed to the fabrication of all-printable devices using a solution shearing printing method. The printed solar cells were highly resistant to water-induced decomposition but they could be easily recycled upon immersion in a citric acid solution and application of heating. Our concept of using abundant natural materials for the fabrication of critical device components is expected to be readily

applicable in a large variety of optoelectronic devices with the aim to decrease their fabrication cost and eliminate environmental pollution caused when these devices reach the end of their lifetime.

Methods

Cellulose nanocrystals preparation procedure. High quality cellulose nanocrystals were obtained through a highly optimized preparation process. The multiple processing steps are as follows: The starting material was a low-cost cellulose pulp dissolved in 64 wt% sulfonic acid (H_2SO_4) solution. The solution was heated while stirred and combined with a Neucel Dissolving pulp feedstock to initiate an acid hydrolysis reaction of the cellulosic pulp. Hydrolysis was quenched after several hours (by the addition of water) and the hydrolysate was then combined with reverse osmosis (RO) water. The cellulose hydrolysate was neutralized by slowly adding 30 wt% sodium hydroxide (NaOH) to obtain a pH of 7. Cellulose NCs were then separated from the wastes (i.e., glucose, sugar oligomers, sodium sulfate salt, and other water-soluble contaminate) by centrifuging the pH neutralized suspension. The solid discharge was diluted with deionized (DI) water (H_2O) and the NCs began to suspend and disperse in the solution. This aqueous suspension was purified using a tangential flow filtration system (implementing hollow fiber tube modules) to separate the salt/sugar contaminants from the NCs. RO water was added throughout the purification process to maintain a NC concentration of 0.5% and diafiltration was continued until the conductivity of the suspension was reduced below $200 \mu\text{S cm}^{-1}$. This purified NC suspension was again centrifuged to remove large particles and unreacted cellulosic materials, while a cartridge-style filter was applied to further remove small unreacted cellulosic materials from the colloidal NC suspension. Additional purification of this suspension was achieved using an ultrafiltration system, which utilized a tangential flow filtration system based on hollow fiber tube modules, to reach a suspension conductivity below $100 \mu\text{S cm}^{-1}$. The highly purified suspension was concentrated up to 3% (using the ultrafiltration system) and was spray dried to achieve the nanocrystalline powder used in the fabrication of the cell.

Preparation of conductive nanocellulose substrates. The nanocrystalline cellulose powder was mixed with NaOH/urea/DI H_2O at a weight ratio of 5.5/13.5/81 and stirred overnight to yield a clear solution. Ammonium metatungstate hydrate ($(\text{NH}_4)_6(\text{PW}_{12}\text{O}_{40}) \cdot x\text{H}_2\text{O}$) POM powder was dissolved in DI water to form 1mM solution. A 2M hydrochloric acid (HCl) aqueous solution was also prepared and added into a POM solution until the pH of the mixed solution was in between 1 and 1.5. The solution was then filtered using a 0.45 mm filter. Next, the POM solution was added onto the cellulose NC solution in an optimized molar ratio to form the conducting ink. A glass solid support was cleaned by sonication in 2% Hellmanex water and isopropanol (IPA) or ethanol (EtOH) solutions for 30 minutes each before being coated with the conducting ink by a solution shearing technique. The influence of coating speed on the CNC characteristics was studied to arrive with best coating quality. Finally, the nanopaper was left to dry overnight in a vacuum chamber at 150°C .

Perovskite solar cell fabrication. A 30 nm thick SnO_2 layer was first deposited on glass/CNC via solution shearing at a speed of $4 \mu\text{m/s}$ and annealed at 130°C for 1 h. Next, PCBM was dissolved in anhydrous chlorobenzene (CB) at 4 mg/mL and coated onto the SnO_2 layer in a nitrogen-filled glove box at a flow rate of $3 \mu\text{m/s}$. After the coating, the substrate was immediately annealed at 70°C for 5 min. The preparation of the RbCsMAFA perovskite solution was as follows: first, the mixed MAFA perovskite precursor solution was prepared by dissolving FAI (1 M), PbI_2 (1.1 M), MABr (0.2 M) and PbBr_2 (0.22 M) in anhydrous dimethylformamide:dimethyl sulfoxide (DMF:DMSO) 4:1 (v:v). Next, the triple cation CsMAFA perovskite was obtained as CsI, predissolved as a 1.5 M stock solution in DMSO, was added to the mixed MAFA perovskite precursor. Finally, the RbCsMAFA perovskite was obtained as RbI, predissolved as a 1.5 M stock solution in DMF:DMSO 4:1 (v:v), was added to the previously prepared CsFAMA triple cation perovskite to achieve the desired quadruple composition. The perovskite solution was coated via convective solution shearing in a two steps program at $3 \mu\text{m s}^{-1}$ and $4 \mu\text{m s}^{-1}$. During the second step, $200 \mu\text{L}$ of CB was sprayed onto the coated substrate 20 s prior to the end of the program. Next, the substrate was placed inside a sample chamber connected to a home-built vacuum-pumping instrumentation. After cooling to room temperature, the hole-transporting material of Spiro-OMeTAD was deposited by coating on top. After perovskite annealing, the substrate was cooled for few minutes and a Spiro-OMeTAD (Merck) solution (70 mM in CB) was coated on it *via* solution shearing at a rate of $2 \mu\text{m s}^{-1}$. The Spiro-OMeTAD was doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209, Dynamo) and 4-tert-Butylpyridine (tBP, Sigma-Aldrich). The molar ratio of the additives for spiro-OMeTAD was: 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and tBP, respectively. Finally, a 160 nm thick anode electrode, consisting of Ag NWs, was coated at a rate of $2 \mu\text{m s}^{-1}$. The Ag NW solution (1 wt% in isopropyl alcohol, IPA) was mixed with a methyl cellulose prepared in propylene glycol/dichloromethane (DCM)/IPA ternary solvents by mixing (hydroxypropyl)methyl cellulose, Zonyl FS-300, and antifoaming agent. The mixture was strongly agitated for 1 h to yield the final Ag NW ink that was used to coat, *via* the solution shearing method, the Spiro-OMeTAD layer.

Photovoltaic cell testing. The current density-voltage (J-V) characteristics were recorded using a Keithley 2410 source unit. The EQE measurements were performed using EQE system (Model 74000) obtained from Newport Oriel Instruments USA. Here, a HAMAMATSU calibrated silicon cell photodiode was used as a reference diode. The wavelength was controlled with a 200-1600 nm monochromator. The voltage scan rate was 5 mV s^{-1} and no cell preconditioning, such as light soaking or extended forward voltage biasing in the dark, was applied before starting the measurement. The cells were masked with a black metal mask to fix the active area and avoid artifacts produced by scattered light. The cell for the statistical (champion) measurement was conducted without (with) antireflective coating and on a 0.25 cm^2 aperture mask. The large area cell was measured on a 1 cm^2 mask. The incident light intensity was adjusted to 100 mW m^{-2} in accordance with standard AM 1.5 reporting conditions.

Stability measurements. Stability measurements were carried out under a full AM 1.5 illumination. The cell was masked (0.25 cm^2) and flushed with nitrogen for several hours before the start of the experiment

in order to remove residual oxygen and water from the environment of an in-house developed sample holder. Next, the cell was measured with a maximum power point (MPP) tracking routine under continuous illumination in nitrogen. The MPP was updated every 10 s by a standard perturb and observe method. The cell's temperature was controlled by a Peltier element in direct contact with the films. The temperature was measured using a surface thermometer located between the Peltier element and the film. To continuously track the evolution of individual J-V parameters, a J-V curve was recorded every 30 minutes.

V_{OC} measurements. V_{OC} measurements were performed using the above LED setup. During the measurement, the cell was left unmasked, at room temperature and under constant nitrogen flow in order to prevent degradation during operation.

Stretching and flexibility tests. The cyclic bending and folding tests were performed using a bending test machine. For the stretching tests, the cell was carefully detached from the solid support and placed in a uniaxial stretch machine for strain test; with one side of the cell was held by the fixed stage and the other side was held by movable stage.

Thin film characterization. The perovskite films were examined using an Osiris field-emission transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV and equipped with an Oxford energy-dispersive X-ray (EDS) detector. The TEM specimens of perovskites were prepared by slow evaporation of dilute solutions deposited under dry conditions on a Formvar-coated holey carbon copper grid. A field emission scanning electron microscope (FESEM, Merlin) was employed to analyze the morphology of the samples using a 3 kV electron beam and an in-lens detector. A neaSNOM microscope, equipped with standard AFM imaging module, was used to obtain topographic images of CNC samples. An area of 800 nm×2 μ m was imaged at a high resolution of 10 nm. The optical properties were measured using a UV–visible spectrophotometer (Varian Cary 5000, Agilent Technologies). XPS and UPS were recorded using a Leybold EA-11 electron analyzer. Material crystallinity was measured by an X-ray diffractometer (D/MAX-2500/PC, Rigaku) using a Cu K α source ($\lambda=1.54\text{\AA}$) operated at 2.4 kW and an HR X-ray diffractometer (Smartlab, Rigaku) equipped with a 2D detector (PILATUS 100K, Rigaku) using a Cu K α source operating at 9 kW.

Declarations

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Author contributions

M.V., P.A and D.D. designed and performed the POM super reduction experiments. B.N.C., B.A. and A.Y.E. synthesized the cellulose nanocrystals. M.V., H.P.K., M.F.M.N., M.F.S. fabricated and characterized devices. W.J.S., F.K.S. performed the AFM, SEM and TEM studies. M.V., M.A.M.T., I.M.C., N.G., A.R.B.M.Y., J.J., M.K.N. designed and supervised the project. M.V. and N.G. wrote the manuscript with contributions from all authors.

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Tables

Table 1. Photovoltaic parameters obtained at forward scan (FS) and reverse scan (RS) directions from the best performing devices shown in Fig. 3a and the J-V curves were recorded at a scan rate of 5 mV s⁻¹. Prior to the experiments, no device preconditioning, such as light soaking or forward voltage bias applied for long time.

Scan direction	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	PCE (%)	R _s (Ω cm ²)	R _{sh} (Ω cm ²)
FS	22.93	1.09	0.789	19.72	7.83	383
RS	22.70	1.09	0.804	19.89	7.32	396