Fabrication of Perovskite Solar Cells with Digital Control of Transparency by Inkjet Printing

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ABSTRACT: Semitransparency is an attractive and important property in solar cells since it opens new possibilities in a variety of applications such as tandem cell configuration and buildingintegrated photovoltaics. Metal halide perovskite has the optimal properties to function as the light harvester in solar cells and can be made as a thin film, while its chemical composition can change its band gap. However, achieving high transparency usually compromises the solar cell's efficiency. Here we report on a unique approach to fabricating semitransparent perovskite solar cells that does not rely on their composition or their thickness. The approach is based on a scalable process, inkjet printing of arrays of transparent pillars, which are composed of inert photopolymerizable liquid compositions and are partly covered by the perovskite. This material can be printed at



specific locations and array densities, thus providing a digital control of both the transparency and efficiency of the solar cells. The new semitransparent device structure shows 11.2% efficiency with 24% average transparency without a top metal contact. Further development including deposition of a transparent contact enabled the fabrication of fully semitransparent devices with an efficiency of 10.6% and average transparency of 19%.

KEYWORDS: polymer-ink pillars, inkjet printing, semitransparent, perovskite solar cells, high efficiency

INTRODUCTION

Metal halide perovskite materials demonstrate a relatively high absorption coefficient, long-range diffusion length, and easy processing, which are attributed to the rapid development of perovskite solar cells (PSCs). These hybrid materials hold special attention compared to other semiconductors employed in solar cells owing to their several distinct properties. Changing the chemical composition of the perovskites can change their optical and physical properties and can also affect their chemical stability.^{1–3} Due to several modifications such as compositional changes, structural alterations, and surface treatments, the power conversion efficiency (PCE) of such solar cells has increased from 3.8% to more than 25% within a decade, which has placed perovskite-based solar cells as gamechangers among other solar cell technologies.^{4–6}

Beyond the PCE and device stability, the perovskite deposition can be performed at low temperatures by simple solution deposition methods. Thus, the perovskites are suitable candidates for the fabrication of high-efficiency, tandem, flexible, light-weight, and semitransparent solar cells.^{7–10}

Semitransparency in perovskite solar cells opens the possibility to use them in building-integrated photovoltaics (BIPV) and tandem cells, following the standard characterization protocols.¹¹ The most common way to fabricate semitransparent perovskite cells is by altering their band gap (perovskite composition) and layer thickness.^{12–16} In this research, we seek a new solar cell structure that is independent of the thickness of the perovskite layer or the perovskite's composition, and that can deliver high efficiency in view of its transparency. Up to now, there are only a few reports on new structures of semitransparent PSCs, with moderate PCEs.^{17,18} Among them is the dewetting technique, which allows formation of a semitransparent perovskite film, but without control over the transparency.¹⁹ By this technique, the solvent is slowly evaporated; as a result, the perovskite crystallization process is slow, which supports the formation of discontinuous perovskite islands. This solar cell structure shows a PCE of 6% and an average transparency (AVT) of ca. 15% for the full device with 10 nm thick Au top contacts.^{19,20} In another approach, a SiO₂ honeycomb scaffold template was utilized by combining self-assembly at the air-water interface and plasma etching. The porous SiO₂ template was prepared by etching the polystyrene while filling the pores with perovskite. The PCE of the cells prepared by this technique is 10.3%, and the AVT of the active layer is 38% as measured without the top contacts.²¹ An additional approach reported by us is based on the mesh-assisted perovskite-grid deposition method, which enables precise control over the transparency, resulting in a PCE of $\sim 10\%$ with 28% AVT for the device without top gold contacts.^{22,23} A drawback of this method is the required delicate control of the required directed wetting, and its

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Figure 1. Schematic illustration of the fabrication of the semitransparent perovskite-based solar cell.

sensitivity to various fabrication parameters such as humidity. In another report, a semitransparent solar cell architecture has been demonstrated using a nanopillar perovskite structure. In this work, a template of anodized aluminum oxide was utilized, which not only provided semitransparency to the device but also improved the device stability. With this nanopillar-based structure, the semitransparent solar cell module reached 9.04% PCE at an AVT of 30.2% with transparent indium tin oxide (ITO) top contacts.²⁴ Although the performance of the cell is very good, this process involves thermal evaporation of the Al, followed by anodization in an oxalic acid solution and etching using phosphoric acid. The Al present between the perovskite nanopillars provides space gaps inside the perovskite layer similarly to our approach where the N-vinylcaprolactam (NVC) ink pillars are printed directly on top of the TiO_2 electrodes by inkjet printing.

The upscaling of solar cells for commercialization could be achieved by inkjet printing, which is being reported for perovskite solar cells with high power conversion efficiencies.^{25,26} However, to the best of our knowledge, the concept of semitransparent perovskite solar cells has not been evolved by the inkjet printing technology for UV-curable polymers.

Here we present a new approach to fabricate semitransparent solar cells with a unique structure, based on digital printing of transparent "holes". These are composed of pillars made of photopolymerizable monomers that can be printed at specific locations and variable array densities, thus providing excellent control over the overall transparency of the solar cells. The inkjet printing process provides several advantages, such as simplicity, short fabrication time, and very low wastage of materials. Another important feature of inkjet printing is its scalability;²⁷⁻²⁹ therefore, it is expected to be suitable for implementation in large-area solar cells. We studied the mechanism of semitransparent cells using intensity-modulated photocurrent spectroscopy (IMPS) and charge extraction. This new approach resulted in an excellent performance of 11.2% efficiency with 27% AVT without the metal contact and a PCE of 10.6% with 22% AVT for cells including a transparent contact.

RESULTS AND DISCUSSION

Here we present a novel and unique structure of semitransparent perovskite solar cell. The main idea is based on printing islands of transparent pillars, while the ink does not damage the photoanode and the perovskite. Figure 1 schematically presents the process for the fabrication of semitransparent perovskite cells. Basically, the photoanode is a mesoporous TiO_2 layer deposited on top of a compact TiO_2 film, while the substrate is fluorine-doped tin oxide (FTO) glass. The ink, which is composed of photopolymerizable material, N-vinylcaprolactam, and photoinitiator (NVC ink), is inkjet printed on top of the mesoporous TiO₂ at specific locations and at a controlled distance. Upon irradiation by UV light for a short time, the monomers convert into a solid polymer in the form of pillars. Following the ink printing, a solution of Cs_{0.2}FA_{0.8}Pb(I_{0.6}Br_{0.4})₃ perovskite is spin-coated on top of the device and spread to the sides of the pillars, which results in the transparency of the film.

It should be noted that since the NVC-ink is deposited by inkjet printing, the pillars' diameter and the spacings between the pillars can be digitally controlled by the printing file design and the nozzle diameter of the printer's cartridge. The pillar diameter depends on the droplet dimensions (determined by the ink properties and wetting behavior) and its fixation on the substrate by the UV irradiation. The spreading of the droplets depends on the surface energy and roughness of the substrate and the surface tension of the ink, and also on its viscosity. In our study, the surface tension of the ink was low (27 mN/m). We evaluated the wetting of the ink by an experiment in which we printed the ink and changed the time until the UV irradiation was performed. We found that the initial pillar diameter is 300 μ m, when the time is passed until the UV irradiation is 20 s. Upon increasing the time to 35 s, the ink pillar diameter increases to 370 μ m and remains constant even for a prolonged time of 300 s. The change of pillar diameter with the time at which the irradiation starts is shown in the Supporting Information, Figure S5. Note that after 6 min,

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Figure 2. (a) SEM image of the printed NVC-ink pattern on mesoporous TiO_2 . Inset—magnification of a specific area that shows the ink pillars. (b) Photograph of the semitransparent solar cell before the Au contact deposition. Inset—optical microscope of the perovskite deposited on the ink. (c) X-ray diffraction pattern obtained for the TiO_2/NVC -ink/perovskite substrate (d). Transmittance measurements of TiO_2/NVC -ink/perovskite—transparency 30.8% and $TiO_2/perovskite$ —transparency 20%.

which is the typical fabrication process in this study, there is no change in the diameter of the pillars.

Figure 2a shows a top-view scanning electron microscope (SEM) image of the printed pillars on top of mesoporous TiO₂. The polymer-ink pattern is uniformly deposited with a diameter of ~300 μ m and distributed evenly on the mesoporous TiO₂ with a distance of ~400 μ m in both X and Y directions. The inset of Figure 2a shows a magnification of the printed and polymerized ink (the ink height is ~600 nm based on the high-resolution transmission electron microscopy (HR-TEM) image as shown in Figure 3). An image of the semitransparent device without the metal contact can be seen in Figure 2b, in which the perovskite film appears uniformly spread on the surface where the ink pattern cannot be recognized. Moreover, it appears from the cross-sectional image (Figure 3) that the perovskite film is present both in the spacings between the pillars and also as a thin-film coating on their top. The X-ray diffraction (XRD) pattern of the perovskite deposited on the ink-printed TiO₂ electrode is shown in Figure 2c. The diffraction patterns indicate interplanar distances of 7.55, 7, 6.21, 4.4, 3.58, 2.78, 2.53, 2.2, and 2.1 Å corresponding to the crystallographic planes (100), (110), (111), (210), (211), (220), and (300), based on the inorganic crystal structure database (ICSD # 243598).^{30,31} A cubic crystal structure that belongs to $P\overline{m}3m$ space group is assigned for the thin perovskite layer.

Figure 2d shows the transmittance of the TiO_2/NVC -ink/ perovskite structure and of the $TiO_2/perovskite$ structures without printed ink. For the perovskite film made from 0.6 M solution, the average visible transmittance (AVT, calculated for the wavelengths 400–800 nm) is 20%. This transparency increased to 30.8% for the NVC-ink structure, resulting from the voids that allow a part of the visible light to pass through the perovskite layer.



Figure 3. Scanning TEM (STEM) cross-sectional image of the semitransparent device. The individual color mapping shows the corresponding elements of the solar cell structure. The NVC-ink is penetrating into the mesoporous TiO_2 , which increases the thickness of the mesoporous TiO_2 in the pillar region, as can be seen from the HR-TEM cross section.

A focused ion beam (FIB) was used to get a cross section of the solar cell and to analyze its structure and elemental chemical composition by HR-TEM (Figure 3). The structure of the solar cell shows a compact TiO_2 , mesoporous TiO_2 , NVC-ink-TiO₂ composite, perovskite, hole transport material (HTM), and Au top contact. Interestingly, following the printing, the monomer NVC-ink spreads into the mesoporous TiO_2 , which forms the TiO_2 -NVC-ink composite. During

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Figure 4. (a) Scanning TEM (STEM) cross-sectional image of the device; the collective color mapping shows the bright spots corresponding to the Cs-richness; (b-d) are the high-resolution lattice scale images obtained in the Cs-rich, the Cs-rich and Cs-deficient interface, and Cs-deficient areas, respectively (the corresponding electron diffractograms are given in the insets).



Figure 5. PV parameters of the NVC-ink PSCs with ~22% AVT. (a) Short-circuit current density, J_{SC} ; (b) open-circuit voltage, V_{OC} ; (c) fill factor (FF); (d) power conversion efficiency (PCE); (e) JV curve of champion NVC-ink device; (f) external quantum efficiency (EQE) spectra of the champion NVC-ink device.

polymerization of the ink, a composite of ink $-\text{TiO}_2$ is formed with a height of 600 nm compared to 200 nm of the *meso*-TiO₂ layer alone. Since the mesopores of the TiO₂ are filled by the NVC-ink, the perovskite cannot penetrate inside the pores in these places (as can be seen in Figure 3 in the case of elements Pb and Ti), which leads to the film transparency. On the other hand, Pb, Cs, Br, and I are observed clearly only in the perovskite areas and not inside the mesoporous TiO₂. Interestingly, the Cs seems to accumulate in specific grains inside the perovskite layer and is not distributed homogeneously in the mixed cation perovskite. To verify this observation, we performed STEM imaging of cross sections of the specific areas in the cell (marked in Figure 4a).

As seen in Figure 4b, the Cs-rich area is composed of $CsPbI_3$ crystalline structure (ICSD # 250744, see Table S3 with the corresponding *hkl* lattice parameters), whereas in the Cs-deficient region (Figure 4d), the crystal planes match the organic–inorganic hybrid perovskite structure [(CH₃)-

 $(NH_3)_2Pb(BrI)_3$, PDF # 01-085-6374]. Figure 4c shows the transition from the Cs-rich to Cs-deficient regions. We predict that the Cs, which is the smaller cation in the perovskite structure, can accumulate in the perovskite layer, which might influence the solar cell performance and stability.

The photovoltaic (PV) parameters for the semitransparent NVC-ink PSCs can be observed in Table S1 and Figure 5a–d. A narrow distribution of the PV parameters is shown for 20 cells (Figure 5a–d), and an average power conversion efficiency (PCE) of 10.2% with 23% average transparency (AVT) is obtained. Importantly, the AVT was measured before the Au contact deposition. One of the interesting parameters is the open-circuit voltage ($V_{\rm OC}$) of these cells. However, there are few reports on perovskite solar cells with high $V_{\rm OC}$ values of similar band gap.^{32,33} Even though the ink height is expected to cause some recombination centers, due to the possibility of direct contact with the HTM layer, the $V_{\rm OC}$ is relatively high, with an average of 1.02 V. The reason for this is mainly the



Figure 6. (a) Charge extraction measurement of NVC-ink and perovskite-grid semitransparent devices. (b) IMPS spectra of the NVC-ink and grid semitransparent devices. (c) Current–voltage curve of the NVC-ink solar cell including transparent contact; inset: image of the champion NVC-ink device including the transparent top MoO_3/Au (10 nm)/ MoO_3 contact. (d) Corresponding AVT and PCE values measured for the NVC-ink devices versus the overall area of the printed polymer pillars.

thin overlayer of perovskite on top of the ink $-\text{TiO}_{2}$, as shown in Figure 3. This thin perovskite layer prevents a direct contact between the HTM and the TiO₂. Our champion device demonstrated a V_{OC} of 1.06V, J_{SC} of 15.9 mA/cm², and fill factor of 66.7%, resulting in a PCE of 11.2% and an AVT of 24% (without the top contact).

Both the JV and the external quantum efficiency (EQE) curves measured for the champion cell are shown in Figure Se,f. The EQE curve follows a similar trend for the absorption of mixed cation mixed halide $Cs_{0.2}FA_{0.8}PbI_{0.6}Br_{0.4}$ perovskite. The small hump in the EQE spectra around 400 nm can be associated with the insufficient absorption of the TiO₂ due to the ink penetration. The integrated J_{SC} obtained from the EQE is 15.8 mA/cm², which is in very good agreement with the J_{SC} measured by the solar simulator (15.9 mA/cm²) and thus supports the reliability of the PV measurement.

In order to better understand the device performance mechanism, charge extraction (CE) and intensity-modulated photocurrent spectroscopy (IMPS) measurements were performed. We compared the results obtained for the current NVC-ink semitransparent devices to our previous reported semitransparent technology of mesh-assisted perovskite-grid structure.^{23,34} A schematic illustration of the semitransparent grid perovskite solar cells can be found in Figure S1b in the Supporting Information. Although the idea behind both structures is to improve the optical transmittance for the PSCs, the structural design is very different. In the case of perovskite-grid structure, the perovskite is deposited on top of the photoanode using a directed assembly process based on using a mesh that creates a perovskite grid on top of the mesoporous TiO₂ electrode. As a result, empty spaces are formed between the perovskite-grid lines, thus providing the transparency on one hand, but on the other hand, these are recombination centers in the device. In the NVC-ink devices, the optical transparency is attributed to the transparent voids that are created by the 300 to 400 μ m m pillars present on the

mesoporous TiO_2 . Note that this polymer is stable and does not react with the perovskite.

Moreover, the perovskite that coats the pillars provides an overlayer (Figure 3) that prevents recombination between the HTM and the perovskite. CE measurements were used previously for several device structures;³⁵ in this method, the device is illuminated for 5 s under open-circuit conditions and then the cell is short-circuited and left in the dark for a certain period of time (i.e., delay time) before closing the circuit and extracting the remaining charges. Figure 6a shows the CE for the two different semitransparent perovskite solar cell structures. The NVC-ink devices show a higher amount of charges left at a certain delay time compared to the grid devices. For example, for NVC-ink devices, the extracted charge is 1.96 \times 10^{-6} C after a delay time of 0.5 s, and it decreases to 3.27×10^{-8} C for 15 s delay time. However, for the perovskite-grid devices, the extracted charge is 4.54×10^{-7} C after a delay time of 0.5 s, which eventually decreases to 1.29 \times 10⁻¹⁰ C after 15 s. It can be concluded that the recombination in case of the NVC-ink device is lower than the recombination in other types of semitransparent solar cells, based on the grid structure reported earlier.²³ This observation is further supported by the IMPS measurements, which provide us the electron transport time. Figure 6b shows the electron transport time as a function of the light intensity for the NVC-ink devices and the grid devices. Clearly, transport is more efficient in the case of the NVC-ink devices. The reason for this lies in the perovskite overlayer coating the pillars, thus enabling a much more efficient transport of charges through the device, in contrast to the grid-based devices, which have direct contact with the HTM and the mesoporous TiO2. To summarize, these measurements show that the newly developed semitransparent devices are efficient in preventing the shunt paths and charge recombination.

In the next step, a transparent contact was deposited on top of the NVC-ink perovskite cells to create a fully semitransparent perovskite solar cell. The transparent contact is

composed of a thin gold film sandwiched between two layers of a metal oxide (i.e., MoO_3). The difference in the dielectric constant of the metal oxide and the gold provides the required transparency, while the gold thickness affects the conductivity but also influences the transparency. Two different gold thicknesses were studied, 10 and 20 nm. Table S2 summarizes the average and the best PV parameters of the fully semitransparent devices. As expected, the 20 nm gold decreases the solar cell transparency to 11%, while the 10 nm gold provides 19% transparency. These transparencies were measured for the full solar cells stuck. The best efficiency observed for the fully semitransparent solar cell was 10.6% with a $V_{\rm OC}$ of 0.99 V, which is very close to the case with nontransparent contact. It is expected that a transparent device would not have a higher J_{SC} value than an opaque device, because light that cannot be absorbed in the active layer is transmitted through the transparent electrode. The mean J_{SC} values are 15.5, 17.0, and 17.6 mA/cm² for FTO/TiO₂/NVCink/perovskite/HTM/Au, FTO/TiO₂/NVC-ink/perovskite/ HTM/MoO₃ (2 nm)/Au (10 nm)/MoO₃ (35 nm), and FTO/TiO₂/NVC-ink/perovskite/HTM/MoO₃ (2 nm)/Au (20 nm)/MoO₃ (35 nm) devices, respectively. However, in the current study, for the semitransparent device we have a thin layer of MoO₃, which leads to an increase in J_{SC} , as we reported earlier,³⁵ and is also in agreement with Chu et al.³⁶ The current-voltage curve and an image of the full solar cell including the transparent contact can be seen in Figure 6c. Once the approach for fabricating a semitransparent solar cells was established, we evaluated the possibility of digital control of the transparency, by changing the pillars' surface density through the printing process. Figure 6d presents the AVT and PCE as a function of the pillar's area fraction. As shown, the higher the pillars' fraction, the higher the transparency and the lower the PCE. Therefore, the target values of PCE and AVT can be easily controlled by the printing parameters while using the same cell structure and materials. It should be noted that the PCE is calculated for the overall cell, which contains also an inactive area (without perovskite). Figure S2 shows a schematic illustration of the calculation of the active area of the cell, while excluding the pillar's area. PCE calculation of the active area only (based on Figure S2) is 13.18% (excluding the ink-pillar area extracted from geometrical model analysis).

It may be argued that achieving 11% efficiency with 22% AVT is low compared to what could be expected for a cell having only 50% of the active area. Theoretically, if one cuts out half of this cell, the $V_{\rm OC}$ will remain the same and the current will drop by a factor of two; therefore, the efficiency of this halved device, assuming the same area A as before, will be x/2%. If the efficiency remains the same x/2%, and if one continues to consider the device to have the original area, the device will have 50% transparency. This evaluation is correct for an ideal cell, for which the $V_{\rm OC}$ and the fill factor (FF) do not change.

However, in fabricating a semitransparent cell in which the spots of inactive area (transparent pillars in our approach) are very small (in the micron range), there is an inherent problem that impacts the cell performance, namely formation of many interfaces, defects, and boundaries. This leads to a significant decrease in J_{SC} . In our case, the V_{OC} values are not affected significantly and are around 1 V, while the FF values are reduced to 66% of that for the nontransparent cell. The low FF value for the ink device is attributed to the reduced perovskite in the effective area of the solar cell structure due to the ink

pillars. Since we use the $Cs_{0.2}FA_{0.8}Pb(I_{0.6}Br_{0.4})_3$ perovskite composition, with an optical band gap of $E_g = 1.74$ eV, the maximum J_{SC} that can be generated by this perovskite is 21.1 mA/cm^{2,37} In the semitransparent cells, the measured Jsc is 15.9 mA/cm². This value is found to be 75% (15.9/21.1 =0.75) of the maximum J_{SCI} meaning a 25% reduction in J_{SC} value. Therefore, in the case of 15.9 mA/cm², the J_{SC} fraction is $\% = 15.9/21.1 \times 100 = 75\%$, and as a result, the theoretical AVT is = 100 - 75 = 25%. For the controlled digital transparency, a set of solar cells were fabricated, varying the ink-pillar area fractions. For a device with 10, 21, 35, and 50%, the J_{SC} values are 16.6, 15.9, 15.6, and 13.8 mA/cm², respectively. The calculated theoretical AVT values for each case are given in the Supporting Information. Figure S3 and Table S4 present the measurements of AVT and J_{SC} values measured for the semitransparent devices vs the fraction of the area of the printed polymer pillars.

CONCLUSIONS

In this work, we developed and investigated a new design of semitransparent perovskite solar cells. Inkjet printing is used in order to print transparent pillars that do not react with the perovskite. The ink is printed on top of a mesoporous TiO_{2} leaving transparent spots, which later on provide the overall transparency to the solar cell. The perovskite is spread in between these spots and also cover them with a thin overlayer. As a result, an efficient semitransparent ink perovskite solar cell is obtained, demonstrating 11.2% efficiency with an AVT of 24% without the contact. The deposition of transparent contact in which gold is sandwiched between two thin MoO₃ layers results in a solar cell with 10.6% efficiency and slightly reduced transparency, 19% AVT. Charge extraction and IMPS show the mechanism behind the efficiency of these semitransparent cells, for which the recombination and electron transport time were measured. This work shows the utilization of inkjet printing as an additive manufacturing technology for the fabrication of highly attractive semitransparent perovskite solar cells. The use of digital printing, which is a scalable process, enables one to precisely pattern and control the transparency while keeping the efficiency high, thus opening the way to scale up fabrication of semitransparent PSCs.

EXPERIMENTAL DETAILS

Materials. All of the chemicals are commercially available, procured, and used for the experiments without further purifications: N-vinylcaprolactam (NVC) (98%, Sigma-Aldrich), diphenyl(2,4,6trimethylbenzoyl)phosphine oxide (TPO) (BASF, Germany), triphenylphosphine (99%, Strem Chemicals), zinc dust (<10 µm, >98%, Sigma-Aldrich), titanium diisopropoxide bis(acetylacetonate) (75 wt % in isopropanol, Sigma-Aldrich), titanium(IV) chloride (TiCl₄) solution (practical grade, FUJIFILM Wako Pure Chemical Corporation, Japan), cesium iodide (99.999%, Sigma-Aldrich), formamidinium iodide (99.99%, Sigma-Aldrich), lead(II) iodide (99%, Sigma-Aldrich), lead(II) bromide (>98%, Sigma-Aldrich), 2,2,7,7-tetrakis-[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMe-TAD) (99.9%, Borun-China), 4-tert-butylpyridine (tBP) (96%, Sigma-Aldrich), lithium bis-(trifluoromethylsulfonyl)imide (99.95%, Sigma-Aldrich), hydrochloric acid (37%, Sigma-Aldrich), Hellmanex (Sigma-Aldrich), and anhydrous solvents like N,N-dimethylformamide (DMF) (99.8%, Acros Organics), dimethyl sulfoxide (DMSO) (99.7+%, Acros Organics), anisole (99.7%, Sigma-Aldrich), ethanol (99%, Fisher Scientific, U.K.), and isopropanol (>99.7%, Daejung Chemicals-Korea). The conducting FTO/glass substrates were procured from Pilkington Pvt. Ltd.

Electrode Preparation. Prior to fabrication of the devices, the FTO conducting glass substrates (sheet resistance ~25 $\Omega \cdot cm^{-2}$) were etched using Zn powder and concentrated HCl solution, obtaining the required electrode conductive patterns followed by cleaning in a soap solution, hellmanex (2% in deionized (DI) H₂O), acetone, and isopropanol each for 20 min, respectively, and placing in an ultrasonic bath. The precleaned FTOs are treated with oxygen plasma for 5 min and then a blocking layer of TiO2 is created by spin-coating (5000 rpm, 30 s) the titanium diisopropoxide bis(acetylacetonate) diluted in absolute ethanol (200 μ L in 1.5 mL). The substrates were calcinated at 450 °C for half an hour. After cooling down, a mesoporous TiO₂ (Greatcell's product: 90T paste, diluted 4 times in absolute ethanol) layer is coated on the substrates using the spin-coater (5000 rpm, 30 s), followed by annealing the substrates at 500 °C for 30 min. After reaching room temperature, these substrates were placed in aqueous TiCl₄ solution (90 mM) and maintained at 75 °C for 30 min, followed by annealing the electrodes at 450 °C for another 30 min. These electrodes were stored in a nitrogen-filled glovebox prior to completing the device fabrication.

Ink Preparation and Printing. The NVC-ink is prepared by taking the NVC monomer (4 gm), a 4 wt % photoinitiator (TPO, 0.16 gm), and 9.2 wt % surface curing agent (triphenylphosphine, 0.368 gm) into a glass vial. After shaking it well for 10 min, the solid mixture is turned into a homogeneous liquid ink. The freshly prepared ink is a viscous solution, diluted further in anisole (1:2 v/v), and this is formulated by using the ink to fill the printer cartridge. The TiCl₄treated substrates are placed on a printer plate, and the inkjet printer "Model: OmniJet100 for DMCDPN" is used for printing the NVCink. During the printing, the cartridge head (10 pL) with one effective nozzle is used among 16 for preventing the mismatching of the dropping location. So the printer head is not tilted vertically during the time of printing the ink. The wettability is found to be good when the ink:anisole ratio is optimized, and the volume of the drop is \sim 4 pL. The printing coordinates were noted in the software. The style for the printing pattern is loaded into the software (Dimatix). During the printing, the cell pitch is 700 μ m and pixel pitch is 25 μ m; both are same in X and Y directions with a jetting frequency of 1000 Hz, and the jetting is controlled by a single-pulse waveform (Figure S6). The solar cell is fabricated on glass/FTO substrates with dimensions of 2.5 $cm \times 2.5$ cm. However, a 2.5 cm $\times 1.5$ cm area is occupied by the TiO₂. With the cell count of 35 and 21 in X and Y directions, respectively, in a single pass, one layer of ink pillars is printed on the entire TiO₂ area within 6 min. At the same time, during the printing of ink, the printer plate and cartridge head were maintained at room temperature. Prior to the printing, the electrode is purged with N2 gas for the elimination of unwanted dust particles from the surface and then NVC-ink is printed as shown in the schematic. After coating a layer of ink pattern on the electrode, without further delay, the substrates were irradiated using ultraviolet (UV) light (a lightemitting diode (LED) lamp with a center wavelength of 395 nm (constant illumination) is used with an intensity of 50 mW/cm^2) for 60 s every time; in total, three ink layers were coated on the electrode.

Device Fabrication. During the device fabrication, on the FTO/ TiO₂ substrates, the deposition of NVC-ink pillars by the inkjet printer is done in the ambient conditions and then the rest of the device fabrication (deposition of HTM and perovskite, metal contact) is done in the nitrogen-filled glovebox. Accordingly, the $\mathrm{Ti}\mathrm{O}_{2}/$ polymer-ink electrodes are taken into the N2-filled glovebox, and a 1.0 M $Cs_{0.2}FA_{0.8}Pb(I_{0.6}Br_{0.4})_3$ solution (in 9:1 DMF and DMSO, aged overnight at 60 °C) is spin-coated (3500 rpm for 30 s, ramp of 6 s) and an antisolvent, chlorobenzene, is dripped over the substrates at the end of 15 s, before the completion of spin-coating. These electrodes were placed on a hot plate at 100 $^\circ \! \hat{C}$ for 30 min. After cooling down to room temperature, the hole transport material (HTM) solution (Spiro-OMeTAD 54 mg in 750 µL chlorobenzene + 13.13 μ L Li salt solution (52 mg lithium bis-(trifluoromethylsulfonyl)imide in 100 μ L acetonitrile) + 21.6 μ L TBP) is spin-coated (4500 rpm, 45 s). In the final stage, for opaque devices, the Au back contact of 70 nm (10 nm at a rate of 0.1 Å/s, followed by 60 nm at a rate of 1.1 Å/s and for the semitransparent devices, a sequential deposition of MoO₃ (2 nm, at a rate of 0.1 Å/s), Au (10/20 nm, at a rate of 0.1 Å/s), and MoO₃ (35 nm, at a rate of 1.1 Å/s) was given using a thermal evaporator by maintaining the chamber at a high vacuum of 10^{-7} Torr.

X-ray Powder Diffraction (XRD) Measurements. XRD measurements for the Glass/TiO₂/NVC-ink/perovskite substrate were performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a secondary graphite monochromator, 2° Sollers slits, and a 0.2 mm receiving slit. At room temperature we recorded the XRD patterns within the range of 5 to 75° 2 θ using Cu K α radiation ($\lambda = 1.5418$ Å), and the measurement conditions were a tube voltage of 40 kV, a tube current of 40 mA, a step-scan mode with a step size of 0.02° 2 θ , and a counting time of 1 s/step.

Transmittance Measurements. The UV-vis measurements for the electrodes before coating the HTM and Au layers were recorded using the Jasco V-670 spectrophotometer. The average visible transmittance (AVT) is calculated by taking the average of the recorded transmittance values (wavelength range of 400-800 nm). During this measurement, the reference beam is left to pass through the air for all of the devices.

SEM. The images of printed polymerized NVC-ink patterns on the TiO_2 surface were taken using a scanning electron microscope (SEM) (Zeiss Supra 55 FESEM, Carl Zeiss Manufacturing Company, Germany). During this measurement, the instrument is operated at 5 kV.

High-Resolution Transmission Electron Microscopy (HR-TEM). High-angle annular dark-field scanning TEM (HAADF STEM, with the accelerating voltage of 300 kV) images were captured with a probe-corrected high-resolution scanning transmission electron microscope, Themis Z, produced by Thermo Fisher Scientific. For this STEM measurement, using the focused ion beam-assisted SEM (FEI Helios NanoLab 460F1 FIB-SEM), the lamella of the NVC-ink device cross section is prepared on a thin copper grid coated with an ultrathin amorphous carbon film on holey carbon. The elemental mapping for the cross section of the device is performed with a Super-X energy-dispersive X-ray spectroscopy (EDS) detector.

Photovoltaic (PV) Characterizations. A Newport system with an Oriel I-V test station and Oriel Sol3A simulator is used for the PV measurements and the solar cell efficiency parameters were extracted for all of the devices. The Class AAA solar simulator was used for determining the spectral performance, uniformity of irradiance, and temporal stability. The system has a 450W xenon lamp, and the output power matched the AM1.5 global sunlight (100 mW/cm²) as the spectral match classifications were IEC60904-9 2007, JIC C 8912, and ASTM E927-05. With the help of a coupled digital source meter (Keithley model 2400), the I-V curves were extracted by applying an external bias to each cell. Before starting the JV measurements, we calibrate the light intensity with the help of a reference Si cell and a power meter. Once the light intensity is 1 sun, we place the solar cell on a black surface and measure the JV with a scan speed of 166 mV/s at room temperature (with no temperature control) using a shadow mask with an aperture area of 0.088 cm².

EQE measurements were done using an IQE200 Newport instrument, containing a tungsten lamp for bias and a xenon lamp with a monochromator for wavelength scan. The measurements (with no-bias light or external voltage) were done in AC mode using a light chopper set at 30 Hz. Before the measurements, the EQE instrument is calibrated using a standard silicon photodiode.

Charge Extraction (CE). CE measurements for NVC-ink and the perovskite-grid devices were performed using an Autolab Potentiostat-Galvanostat (PGSTAT) with a FRA32M LED driver equipped with a white light source. For the data collection and analysis we have used the Nova 1.1 software program. During the measurement, in the first step the cell was discharged for 2 s in the dark followed by 2 s of 0.7 sun illumination. In the next step, the light is shut down and the system kept waiting for a certain time (delay time) before reconnecting and collecting the remained charges. The measurements have several cycles, wherein each cycle has a different delay time between 0.5 and 15 s.

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Intensity-Modulated Photocurrent Spectroscopy (IMPS). The IMPS measurements for the NVC-ink and perovskite-grid devices were performed using the Autolab Potentiostat-Galvanostat (PGSTAT) with a FRA32M LED driver equipped with a white light source. For the transport lifetime data collection, we have measured the electrochemical impedance spectroscopy (EIS, Nyquist) plots using the Nova 2.1.1 software program. The Nyquist plots were recorded every time by illuminating the cell (at short-circuit conditions) with a constant white light. For these measurements, the intensity of the light is modulated between 0.1 and 0.7 sun.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c04407.

Includes schematic representations of ink-pillar and perovskite-grid designs of the perovskite solar cells; active area calculations; average PV parameters of the semitransparent cells; *JV* curves/PCE-parameters obtained for devices in forward/backward biases; and wetting time vs ink-pillar diameter plots (PDF) AVT from avg and photon flux (XLSX)

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Notes

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