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# Solar Cells with High Short Circuit Currents Based on CsPbBr<sub>3</sub> Perovskite-Modified ZnO Nanorod Composites

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#### Abstract

3-D all-inorganic perovskite solar cells have been built using vertically aligned conductive zinc oxide nanorods as the electron transport layer and optical waveguide. Yttrium doping improved the conductivity and hence the electron transportation of the ZnO achieving a threefold improvement of the solar cell efficiency. The vertically aligned nanorods act as optical waveguides and a scaffold, which improved photoabsorption of the perovskite semiconductor by increasing layer thickness. Our device structure was completed with an exfoliated multilayer graphite back contact for effective hole-extraction. The ZnO was most significantly modified by nanometre scale coatings of TiO<sub>2</sub> in order to passivate the surface and reduce charge recombination, as measured by photoluminescence spectroscopy. This led to greatly improved charge transfer. This strategy led to an overall nine times enhancement in the solar cell efficiency, yielding a competitive top value of 5.83%. More importantly, the all-inorganic solar cells demonstrated excellent stability, showing no decline in initial performance after 1000 hour storage in ambient conditions. This work presents yttrium doped ZnO nanorods as a suitable replacement for mesoporous TiO<sub>2</sub>, achieving a high short circuit current of 10.5 mA cm<sup>-2</sup> for CsPbBr<sub>3</sub> perovskite devices.

Keywords: Inorganic perovskite, ZnO nanorods,  $TiO_2$  coating, Graphite, ambient synthesis

# **1. Introduction**

Over the last decade a tremendous rise in efficiency has brought organic-inorganic hybrid perovskite solar cells (PSCs) to the frontier of renewable energy research.<sup>1–3</sup> However, the poor stability of the material under hot and humid conditions has led to the burgeoning field of inorganic perovskite cells, replacing various organic cations with cesium.<sup>4</sup> In the few years since conception,<sup>5</sup> efficiency in such devices has risen to 18.4% using CsPbI<sub>3</sub>,<sup>6,7</sup> and recently passed 10.9% using wide band gap, CsPbBr<sub>3</sub>.<sup>8</sup> Crucially, these devices display better long term stability in high humidity and temperature testing. Thus far, nearly all these devices have used mesoporous TiO<sub>2</sub> as electron transport material (ETM) with some notable exceptions, such as ETM free and interfacial quantum dot devices.<sup>9,10</sup> High charge mobility and tuneable morphology makes ZnO a promising alternative, leading to its wide application to hybrid PSCs.<sup>11,12</sup> So far, the performance of this material has been significantly enhanced using dopants.<sup>13</sup> Surface charge recombination has been effectively reduced by coatings of a barrier layer, such as MgO.<sup>14</sup> For inorganic PSCs, ZnO thin films have been employed as ETM in a limited capacity.<sup>6,15</sup> leaving more exotic morphology unexplored.

In a typical hybrid PSC, doped 2,2',7,7'-tetrakis (N,N'-di-p-methoxyphenylamine)-9,9'spirobifluorene (spiro-MeOTAD) and noble metal contacts are used as hole transport materials (HTMs). These materials are not only expensive ( $\sim$  \$350/g and  $\sim$  \$50/g respectively),<sup>16</sup> but also contribute significantly to device degradation.<sup>17</sup> For this reason, many HTM-free PSCs have been designed, including amorphous carbon contacts.<sup>18,19</sup> In this work, vertically aligned, conductive zinc oxide nanorods (NRs) have been applied for the first time to inorganic PSCs with CsPbBr<sub>3</sub>. These structures have been previously shown to act as optical waveguides, suitable for light trapping as well as charge transfer.<sup>20</sup> Yttrium was selected as a dopant as past work revealed its role in conductivity gain: Increasing both dopant density and charge mobility.<sup>21</sup> Using a two-step deposition method the photoactive perovskite showed good infiltration between the NRs, yielding layers with very high photoabsorption. Modification of ZnO with Y doping and TiO<sub>2</sub> coating gave record short circuit currents for CsPbBr<sub>3</sub> of >10 mA cm<sup>-2</sup>, in an efficient optical wave-guide and charge transfer system. This allowed the device to be highly competitive with the widely used mesoporous TiO<sub>2</sub>, with a champion efficiency of 5.83%. These devices benefit further still, from a highly simplified liquid phase exfoliated (LPE) multilayer graphite, synthesised by one-step probe sonication and drop cast directly onto the perovskite. Highly stable and conductive graphite represents one high quality back contact material for PSCs.

#### 2. Experimental Method

# 2.1 ZnO NR Synthesis on FTO substrates

All chemicals used were purchased from Sigma Aldrich with no further purification. Fluorine doped Tin Oxide (FTO) coated conductive glass was cut into 12 by 25 mm. The edges of the substrates were etched to remove FTO using 2 M HCl and Zn powder. This was followed by cleaning via sonication in acetone, isopropanol and DI water for 15 minutes in each solvent and subsequent drying in air. ZnO NRs were grown by a typical chemical bath deposition method, CBD.<sup>22</sup> The substrates were first seeded with spin coating (800 RPM for 90 seconds followed by 30 seconds at 2000 RPM) with 0.1 M zinc acetate solution in DI water and 0.6 wt% polyvinyl alcohol. The sample

was annealed in air at 500°C for 20 minutes to form zinc oxide seeds.<sup>22</sup> NR growth was achieved by CBD, using a 20 mM equimolar solution of zinc nitrate and hexamethylenetetramine. Doping of yttrium was introduced to the growth solution with yttrium nitrate solution (0.2 mM). Substrates were placed face down in the solution and left for 16 hours at 85°C to achieve ~1  $\mu$ m NR length. The sample was rinsed with DI water, dried and annealed at 500°C for 30 minutes. The length of the NRs was finely controlled with mild acid treatment (0.1 M HCl), followed by quenching in DI water after the specified duration had passed. To expose the FTO contact, ZnO was removed from an area of 4 × 12 mm<sup>2</sup> with 2 M HCl solution.

## 2.2 Formation of TiO<sub>2</sub> shell on ZnO NR cores

Layers of amorphous  $TiO_2$  were deposited on the ZnO NRs via a successive layer adsorption and reaction technique (SLAR). A 10 mM Titanium (IV) isopropoxide (TTIP) solution was first prepared in isopropyl alcohol (IPA). The NR arrays were submerged in this solution and soaked for 15 minutes. This allowed TTIP in the solution to be adsorbed onto the surface of the rods, which were then dipped for 30 seconds in IPA to remove any excess, followed by dipping in DI water to convert the TTIP into  $TiO_2$  via the following reaction.

$$Ti(OCH(CH_3)_2)_4 + 2H_2O \rightarrow TiO_2 + 4(CH_3)_2CHOH$$
(1)

This deposition sequence is referred to as one dip cycle. The thickness of the  $TiO_2$  shell was controlled by the number of cycles applied. Finally, the substrates were annealed at 500°C for 30 minutes to convert amorphous  $TiO_2$  into anatase phase, forming a core-shell NR structure with  $TiO_2$  shell on ZnO NRs.

#### 2.3 CsPbBr<sub>3</sub> Deposition between TiO<sub>2</sub>-ZnO Core-shell NRs

The inorganic perovskite, CsPbBr<sub>3</sub>, was deposited on and between the TiO<sub>2</sub>/ZnO core-shell NRs by a two-step method. Firstly, PbBr<sub>2</sub> was spin coated upon the rods using a 1 M solution in DMF, held at 100°C for one hour prior to coating, while the substrates were maintained at 90°C. The use of hot solution and sample is to prevent the formation of large crystals and ensuring they were dry. Spin coating was performed at 2500 RPM for 30s. The samples were dried at 90°C for one hour before submerged in a 0.07 M CsBr methanol solution for 40 minutes at 50°C, reacting to form crystallised CsPbBr<sub>3</sub>.<sup>23</sup> The substrates were then soaked in IPA for 5 minutes to remove any excess CsBr and dried in air.

#### 2.4 Multilayer Graphite Ink Synthesis and Casting as Back Contact

Graphite ink was produced by liquid phase exfoliation (LPE) through sonication of graphite powder. The dried graphite powder is dispersed in chlorobenzene at a concentration of 10 mg/ml using a 300W sonic probe for 40 minutes at 80% power. Residual particles were removed by centrifuge method. The dispersion remained stable for weeks. Glass templates with fixed area were used to pattern back contacts, after drop casting of graphite, resulting in an effective solar cell area of  $\sim 0.1 \text{ cm}^2$ . The graphite coated glass was used as the cathode of the solar cell. The assembled solar cells were annealed at 250°C for five minutes to remove residual solvent and to improve the adhesion of graphite. The full experimental procedure for cell construction is summarised in Scheme 1.

# 2.5 Structural and Physical Characterization

ZnO NR, TiO<sub>2</sub> coating, CsPbBr<sub>3</sub>, and graphite morphologies were determined using scanning electron microscopy (SEM, Leica Stereoscan 420) along with EDX element analysis using INCA software (Oxford Instruments). Film thickness and surface morphology were analysed using Image J software (National Institutes of Health, USA) with SEM images of the cross section and surface respectively. Transmission electron microscopy (JEOL JEM1400-Plus) was used to confirm the multilayer structure of graphite and to measure TiO<sub>2</sub> layer thickness. The crystallographic properties of each layer, and full device were characterised by powder x-ray diffractometer (XRD, Siemens D500).

# 2.6 Efficiency and Optoelectronic Measurement

Solar cell performance was analysed under illuminated conditions using a calibrated 100 mW/cm<sup>2</sup> solar simulator (Oriel LCS-100, Newport) with built-in AM 1.5G filter, along with Palm Sens 3 (Palm Sens BV) electrochemical controller at a typical scan rate of 20 mV/s. The same light source and controller were used for illuminated Electrical Impedance Spectroscopy (EIS) under short circuit conditions with sinusoidal AC bias of 10 mV at frequencies varying from 50,000 to 0.1 Hz. The results were processed with PSTrace 4.5 (Palm Sens BV). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha using Al K $\alpha$  source) was used to determine valence band position and surface composition. UV-Vis absorption spectroscopy was performed using a spectrophotometer (Thermospectronic UV 300) to determine the optical band gaps of the materials. The incident photon-to-current conversion efficiency (IPCE) was measured using a 300 W xenon lamp with a monochromator and a digital multimeter (GW Instek GDM-8341). The light intensity was

characterized using a silicon photodiode sensor and optical power meter (Newport). Photoluminescence spectroscopy was used to confirm the presence of CsPbBr<sub>3</sub> along with its passivation effect at the ZnO/CsPbBr<sub>3</sub> interface, with a fluorescence spectrometer (PerkinElmer LS-45). Finally, bandgap energy was measured using an Ocean Optics USB UV-Vis spectrometer and an ISP-REF integrating sphere and a powder MgO reference, equipped with an inbuilt 300 nm  $\leq \lambda$  $\leq 1000$  nm tungsten-halogen lamp.



Scheme 1: The experimental procedure for the all inorganic perovskite solar cell construction including ZnO NR synthesis and TiO<sub>2</sub> coating followed by CsPbBr<sub>3</sub> and graphite deposition.

# 3. Results and Discussion

# 3.1 Device Morphology and Crystallography

The novel device design which combines ZnO NRs with CsPbBr<sub>3</sub> for the first time can be seen in schematic, Figure 1A, alongside a typical cross sectional SEM image of the solar cell. The layers of different materials are visible in the image, orthorhombic CsPbBr<sub>3</sub> crystal texture can be seen, penetrated by ZnO NRs with sheet like layers of exfoliated graphite on the surface. Images representative of the full junction at lower magnification show good contact between the CsPbBr<sub>3</sub> and graphite layers, Figure S1. The perovskite phase shows good infiltration into the ZnO layer, indicating good contact at the interface which likely facilitates rapid charge transfer. The thickness of ZnO/CsPbBr<sub>3</sub> together is ~1.7  $\mu$ m providing an effective light absorbing layer, far thicker than typical planar, and mesoporous CsPbBr<sub>3</sub> solar cells.<sup>9,18</sup> Here, the thickness of the CsPbBr<sub>3</sub> has to be larger than the length of the ZnO NRs, otherwise, a short circuit between anode and cathode will form. ZnO NRs have shown evidence of acting as optical waveguides, trapping light in the geometry and feeding it into the photoactive layer,<sup>20</sup> a further advantage over mesoporous TiO<sub>2</sub>.<sup>24</sup> The graphite back contact acts as a hole extraction layer, which was drop cast to a thickness of ~50 $\mu$ m. Most reports use a commercial carbon paint consisting of graphite, carbon black and stabilising agents, applied typically by doctor blading.<sup>19,25,26</sup> By annealing at 250°C the graphite sheets improve direct contact with CsPbBr<sub>3</sub> crystal surface, providing channels and larger surface area for hole transport.



Figure 1: (A) The solar cell schematic alongside a cross sectional SEM image of the cell, (B) The energy level diagram of the layered device. (C) A top down SEM of typical perovskite film quality and finally (D) The powder XRD of the device.

Additional features to the solar cell architecture, not directly seen in the SEM in Figure 1A, are the Y doping and TiO<sub>2</sub> coating of the ZnO NRs. Y doping was used to increase the conductivity of the NRs as an n-type dopant, increasing the electron conductivity.<sup>27</sup> The electronic structures of the solar cell is shown in Figure 1B. The conduction and valence band positions of ZnO and TiO<sub>2</sub> were determined by x-ray photoelectron spectroscopy (XPS)

displayed in Figure S2 combined with UV-Vis absorption spectroscopy.<sup>21</sup> The other values were found in literature as expanded in Table S1. By employing the coating strategy, electron transfer from CsPbBr<sub>3</sub> to ZnO conduction band becomes more favourable via the better aligned conduction band of the TiO<sub>2</sub> shell. Meanwhile, the valence band alignment also leads to significant hole blocking. The suitable work function allows the graphite to select and transport holes effectively, blocking electrons via a Schottky barrier.<sup>28</sup> The top-down SEM image of the CsPbBr<sub>3</sub> layer in Figure 1C), shows reasonably large perovskite grains (0.85µm), vital for good performance due to recombination at grain boundaries.<sup>26</sup> The CsPbBr<sub>3</sub> was confirmed as the orthorhombic phase (PDF # 18-0364) by XRD (Figure 1D) with nearly all peaks indexed by this pattern. Small peaks occurring at ~ 12, 18 and 29° are contributed from the tetragonal CsPb<sub>2</sub>Br<sub>5</sub> (PDF # 25-0211) due to the incomplete formation of CsPbBr<sub>3</sub>. The presence of small quantities of CsPb<sub>2</sub>Br<sub>5</sub> is common in two step depositions.<sup>19,29</sup> It can help to reduce photoluminescent energy loss due to its indirect band gap.<sup>30</sup> Other observed peaks confirm the overall structure of the solar cell, corresponding to graphite, FTO and ZnO NRs with growth in the favourable 002 direction (PDF # 361451). The TiO<sub>2</sub> coating is too thin to be observed by XRD.

# **3.2 Liquid Phase Exfoliated Hole Transport Material**

The graphite based dispersions employed to complete the structure of the solar cell, are elegant in their simplicity. Its compatibility with hole-transport materials and perovskite makes dispersed graphite an ideal back contact material.<sup>31</sup> In Figure 2A, the stability of the colloid is observed over time showing lack of aggregation even after a month. Chlorobenzene was used as a suitable solvent for C60 and graphite,<sup>32,33</sup> due to better matching Hansen solubility

parameters and is able to hold higher concentration in dispersion.<sup>34,35</sup> It is for this reason, it was



Figure 2: (A) The stability of the exfoliated ink over time, up to 28 days. (B) A TEM image of few-layer graphite and multilayer graphite along with inset (C) A typical SEM of the drop cast material.

selected in this work for liquid phase exfoliation of graphite. Furthermore, basing the ink purely on graphite flakes leads to an environmental advantage over carbon black, which is a known pollutant.<sup>36</sup> Evidence that the ultrasonication of graphite leads to the exfoliation of fewlayer graphite in the ink can be found in the TEM and SEM images, Figure 2B and C respectively. Flakes of various thickness are observed, with faded few-layer graphite observable in the top left, and a multilayer sheet on the right.

Despite the thickness of the flakes, the layers are clearly offset and folded from each other indicating strong exfoliation under the ultrasonic treatment, without using complicated graphite oxidation and reduction processes.<sup>37,38</sup> The flakes vary in size from 180 - 1500 nm, with an average of 500 nm taken from a survey of flakes found in Figure S3 (Supporting information), typical of the exfoliated graphite.<sup>39</sup> The SEM image, shown in Figure 2C, confirms smooth morphology of the drop cast layer. This is reflected in the low sheet resistance of the films, measured to be 1.64  $\Omega/\Box$  with a resistivity of 0.014  $\Omega$  cm, using a four point probe. This resistance is lower than the commercial FTO glass used (7  $\Omega/\Box$ ). As far as the authors are aware, this is the first time a ultrasonicated LPE graphite ink has been applied as cathode back contact in a perovskite solar cell. Although, it has been used to enhance the electron transportation on the TiO<sub>2</sub> anode in perovskite cells.<sup>40,41</sup>

#### **3.3 Yttrium Doping and Length Control of Electron Transport Material**

In this work, the electron transport layer was enhanced by yttrium doping, which had both a morphological and electronic effect on the ZnO NRs. The 1% molar addition of  $Y^{3+}$  in the growth stage has been found to be optimal for solar application in previous work,<sup>27</sup> leading to increased conductivity and more favourable geometry with higher aspect ratio.<sup>20</sup> The true molar concentration of Y in the NRs was determined by inductively coupled plasma mass spectroscopy, to be 0.1% with respect to Zn.<sup>27</sup> The cross sectional SEMs of ZnO / CsPbBr<sub>3</sub> layers based on pristine (C), and Y doped (A,B,D) NRs based are shown in Figure 3. The corresponding ZnO NR layers with the CsPbBr<sub>3</sub> layer removed are shown in Figure S4A-D for comparison, showing the difference in the ZnO NR length. In samples A, B and D, NR length was controlled by acid washing for 0, 10 and 30 s with achieved layer thickness of 1195, 917 and 625 nm, respectively. The samples are named as Y1195, Y917 and Y625 respectively. The ZnO NR relative lengths are implied by powder XRD of the devices, whereby the intensity of the z axis peak indicates greater abundance of the vertically orientated lattice plane.<sup>42,43</sup> Here, the 002 ZnO peak at 34.5° increases in intensity from the Y625 sample up to Y1195, the patterns are found in Figure S5.

The unwashed Y doped NRs (1195 nm) grew ~400 nm longer than the pristine sample (808 nm) due to the opposing partial charge of the NR sidewall planes in basic solution, to the complex formed by dopant ions.<sup>27</sup> This in turn led to a significant increase in light absorption, Figure 3E), above the band edge of CsPbBr<sub>3</sub> (<540 nm) due to a thicker supporting scaffold of the NRs. This is a consequence of the thicker perovskite layer absorbing more light. This would increase the light absorption efficiency and lead to a higher population of photogenerated charge carriers in the photoactive layer. Reducing the thickness of the ZnO layer, predictably, led to reduced absorption, reaching a minimum with 30s acid treatment as the NRs were significantly shorter than the pristine sample. However, increased film thickness can result a higher charge recombination, which is the main limit of most thin film solar cells. Through embedding the perovskite in conductive ZnO NRs, such limitation can be effectively overcome. On the other hand, the perovskite coating must be thicker than the length of the ZnO NRs to avoid short

circuit. If the NRs protrude from the surface of the CsPbBr<sub>3</sub> they will directly contact the graphite layer resulting in the potential of strong reverse flow of current. This effect can be seen in Figure 3A, and most clearly in Figure S6, top down SEM images of the deposited perovskite films.



Figure 3: (A-D) SEM cross sectional images of the samples, A,B and D were the yttrium doped samples, labelled after the NR length. Y917 and Y625 had their length controlled by acid washing, the length of the pristine sample was found to be 808 nm. (E) The UV-Vis absorption spectra of the samples and F the UV-Vis reflectance.

The visible NRs have been circled in red and show more frequently the greater their length. The sample Y1195 shows the most and therefore has the greatest chance of short circuit and back current.

Some morphological differences are observed in Figure S6, despite similar grain sizes measured and recorded on the images themselves. The sample Y625 appears to have a smoother and more interconnected perovskite layer than the rest of the samples. This is likely due to the separation of the grains caused by the longer NRs, leading to the prominent orthorhombic shapes in Y917. This could be an issue for hole transfer to the graphite, but electron transfer to adjacent ZnO would be unharmed.

A visual comparison between Figure S4A-D and Figure 3A-D shows the CsPbBr<sub>3</sub> successfully filling the gaps between the NRs. Despite this some voids remain visible in Figure 3, circled in red. The dark spots imply spaces in the perovskite layer, likely unfavourable to the full cell performance, as recombination centres with poor charge transfer. The thinner the NR layer the fewer voids are observed, with Y625 showing nearly none. This is argues in favour of controlling the NR lengths with acid treatment, potentially leading to fewer voids and more effective charge transfer. The optoelectronic effect of dopant ions on the ZnO NRs can be seen in Figure S7, where the direct band gaps of the materials were measured using Tauc plots.<sup>44</sup> The reproducible value of 2.29 eV for CsPbBr<sub>3</sub> was obtained in agreement with literature,<sup>26</sup> along with a small red shift in band gap energy with Y doping corresponding to the absorption onset of ZnO. This shift is due to the effect of interstitial yttrium atoms, introducing electronic states in the band gap.<sup>21</sup> Though a minor optical effect, the n-type doping has a strong influence on the NR conductivity as indicated by Table 1, with samples Y917 and Y625 showing a four and

two times reduction in series resistance, R<sub>s</sub>, in comparison to the pristine sample respectively. This in turn leads to higher short circuit current, J<sub>sc</sub>. Furthermore, the new E<sub>F</sub> position in the ZnO with yttrium doping, raises the  $n-E_F$  in the intrinsic perovskite phase yielding greater energy difference between the quasi levels.<sup>21,45</sup> This led to larger open circuit voltage,  $V_{oc}$ , in these samples. Due to the synergistic improvement of Voc and Jsc, the efficiency of Y917 showed a greater than three-fold enhancement over the Pristine sample. Therefore, the optimum length of NRs for perovskite solar cells is ~917 nm; striking a balance between light absorption and short circuit recombination occurring from ZnO, graphite contact. Also apparent is the sensitivity of the ZnO film thickness, the longest Y1195 sample showed only a slight increase over Pristine due to the high R<sub>s</sub> value, low FF and low V<sub>oc</sub> possibly due to direct contact of the NRs with the graphite counter electrode. This will cause a significant back current and reduction of shunt resistance, R<sub>sh</sub>, responsible for the cells diodic response. Reduced R<sub>sh</sub> leads to a collapse in Voc as observed in the table.<sup>46</sup> The Voc seems to increase with reduced NR length, confirming this suggestion as the separation between ZnO and graphite improves R<sub>sh</sub>. Almost as destructive to performance is the over shortening of the NRs, where photocurrent is significantly stifled due to the poor light absorption found in Figure 3E.

The UV-Vis reflectance spectra of the ZnO / CsPbBr<sub>3</sub> layers were also measured, with the results displayed in Figure 3F. The step at 530 nm indicates the onset of reflection from the CsPbBr<sub>3</sub> as it stops effectively absorbing at energies below its optical band gap. The reflectance at wave-lengths below 530 nm show evidence of light trapping, as the sample with greatest absorption, Y1195, reflects the least light. This is likely due to the optical wave guiding properties of these nanostructures.<sup>20,47</sup> The longer the waveguide, the more reflections and

emissions off side walls occur, with greater opportunity for light to be absorbed by CsPbBr<sub>3</sub>. Conversely, in the short rods there is less chance of side wall reflections and emission, hence the device behaves more like planar cell with increased reflectance.<sup>48</sup> This side wall reflection could be further improved due to the increase of refractive index by doping in ZnO. The normal values for refractive indices are 2.0 for CsPbBr<sub>3</sub> 1.9 for ZnO and 2.0 for Al doped ZnO, therefore, doping would reduce optical impedance and increase the side emission intensity.<sup>49–51</sup> Secondly, the fractional power loss for guided modes is strongly dependant on the nanowire radius, with thinner wires causing greater loss in field intensity.<sup>52</sup> The effect of yttrium on the growth of the NWs has been previously reported to stifle lateral growth, reducing the radius to 40 nm would mean greater losses allowing light to better leak out into the cell.<sup>27</sup> Conversely, undoped ZnO NRs with radii of 100 nm would lead to >90% power retention, confining the light in the wire to reflect back out again.<sup>52</sup> Greater light trapping and delivery to the perovskite by doped ZnO NRs is another reason for the higher *J<sub>sc</sub>* in the doped samples.

| Sample   | η / % | $J_{sc}$ / mA/cm <sup>2</sup> | $V_{oc}$ / V | FF   | $R_s/\Omega$ |
|----------|-------|-------------------------------|--------------|------|--------------|
| Pristine | 0.63  | 1.92                          | 0.83         | 0.39 | 178          |
| Y1195    | 0.83  | 3.56                          | 0.75         | 0.31 | 193          |
| Y917     | 2.10  | 4.02                          | 0.90         | 0.58 | 36           |
| Y625     | 1.22  | 2.54                          | 0.95         | 0.51 | 81           |

Table 1: Solar cell performance and IV curve parameters, along with series resistance  $R_s$ . All parameters were derived from forward scans, full scans can be found in Figure S8.

# 3.4 Improved Charge Transfer from TiO<sub>2</sub> Coating

The Y doped ZnO NRs were further modified by coating with TiO<sub>2</sub> via a simple dipping method in order to improve the PCE of the perovskite solar cell further, reducing charge recombination at the ZnO surface. The morphological effect of the TiO<sub>2</sub> begins to be visible under SEM after three dip cycles (Figure 4A-D) leading to the presence of some surface roughness and bumps. This becomes more prevalent with further cycles up to 10 dips, where the rods themselves begin to be masked by surface coating and a significant amount of cross linking can be seen. The NRs in Figure 4A-D show no significant differences in diameter despite some statistical outliers, as shown in histogram Figure S9. The larger NRs occur due to the convalescence of growth together, a side effect from the CBD synthetic method.<sup>53</sup> Methods that yield more uniform size distributions and greater vertical alignment were considered, such as chemical vapour deposition, CVD. However, this is less easily scaled up for commercial

application.<sup>54</sup> In order to confirm the presence of coating and measure its thickness, TEM was used in Figure 4E, on the sample with 3 dip coatings where a clear, lighter, outer layer is observed. The thickness of this layer was determined to be 5.1 nm thick and homogenous over the rods, but this could be the result of diffraction effects. Therefore, it was further evidenced by EDX measurements, Figure S10. Though TiO<sub>2</sub> coating is a common strategy to improve ZnO NR performance, to the authors' knowledge this is the first time the thickness of said coating has been controlled at the nanoscale to optimise the performance of perovskite solar cells.<sup>55,56</sup>

In order to further confirm the presence of  $TiO_2$  on the NR surface XPS was used to analyse the surface composition. The survey scan displayed in Figure 4F clearly shows the presence of Zn, Ti and O on the substrate surface. In order to investigate the oxidation state of Ti, a high resolution scan was performed on the 2p region, from 445 to 475 eV. Unsurprisingly the titanium was confirmed to be in Ti<sup>4+</sup> state, with no obvious peak doubling or widening due to the presence of Ti<sup>3+.57</sup> This confirms the presence of TiO<sub>2</sub>.



Figure 4: (A-D) The top down SEM images of the ZnO NRs post  $TiO_2$  coating, before perovskite deposition, with increasing dip cycles from 0, A to 10, D. (E) The TEM of the 3 dip cycle coated ZnO NRs, used to measure the thickness of the  $TiO_2$  layer. (F) Shows the XPS survey scan of the  $TiO_2$  layer, and (G) shows a high resolution scan of 450-475 eV.

Box plots of the solar cell parameters are shown in Figure 5A-D, each point represents 5 or more different cells measured with varying TiO<sub>2</sub> coatings. The best performing 3 dip cycle NRs were confirmed with 27 cells in order to confidently reproduce data. The median value of efficiency (Figure 5A) increases dramatically for the lightest coating of 5.1 nm thickness, by a factor of over two. The mean average value of this coating is  $2.93 \pm 0.2$  %, giving consistent efficiency over various samples. This increase corresponds strongly with a leap in  $J_{sc}$  due to passivation and hole-blocking effects at the YZnO/CsPbBr<sub>3</sub> interface.<sup>14</sup> One disadvantage of ZnO as the ETM is the high recombination rate at the aforementioned interface, as electrons are free to combine with CsPbBr<sub>3</sub> valence band holes. A thin layer of TiO<sub>2</sub> significantly reduces this process, acting as a hole blocking layer. Furthermore, this layer causes better contact between the ZnO and perovskite, passivating surface traps on the NR surface. This tactic is vital for the function of ZnO NR devices, with the record breaking performance of this material in a perovskite solar cell achieved by Cao *et al.* using MgO for passivation.<sup>14</sup> TiO<sub>2</sub> coating also led to a monotonic increase in  $V_{oc}$ , Figure 5C, due to the more positive position of the TiO<sub>2</sub> conduction band and  $E_F$ . However, for 6 and 10 dip cycles this effect was accompanied by reduced  $J_{sc}$  due to the increased series ( $R_s$ ) and charge transfer resistance ( $R_{ct}$ ) measured by EIS, Table 2.

| Sample   | $R_s/\Omega$ | $R^{z}_{ct}/\Omega$ | $C^z/\mathrm{nF}$ | $R^{p}_{ct}/\Omega$ | $C^p/\mu F$ |
|----------|--------------|---------------------|-------------------|---------------------|-------------|
| Pristine | 1339         | 2909                | 0.721             | 9585                | 110         |
| Y Doped  | 398          | 2190                | 15.6              | 2231                | 142         |
| 3 dips   | 0.782        | 1682                | 9.42              | 2212                | 186         |
| 6 dips   | 135          | 1730                | 8.40              | 2473                | 951         |
| 10 dips  | 249          | 3542                | 59.7              | 4498                | 356         |

Table 2: EIS results of the equivalent circuit parameters, the raw data, equivalent circuit and simulated fits are found in Figure S11.



Figure 5: (A-D) Show the solar cell parameters with varying thickness of TiO<sub>2</sub> coating.

The full impedance spectra can be found in Figure S11A, displaying two distinct semicircle regions, the high frequency region is typically assigned to charge selective contacts, and the low frequency to the recombination and capacitance of the perovskite material.<sup>58</sup> Combining this with the equivalent circuit Figure S11B, the high frequency arc parameters were assigned to the ZnO/CsPbBr<sub>3</sub> interface,  $R^{z}_{ct}$ ,  $C^{z}$ . The low frequency parameters were assigned to the perovskite material itself,  $R^{p}_{ct}$ ,  $C^{p}$ . Both Y doping and TiO<sub>2</sub> coating have a dramatic effect on the cell  $R_{s}$ , due to the optimisation of ZnO.



Figure 6: (A) Typical IV curves (forward scan) of various preparation conditions. (B) The IPCE of the samples along with the integrated photocurrents. (C) The photoluminescence spectra of the samples, with a 400 nm exciting wavelength. (D) The stability of the performance of the solar cell over time.

As previously described the increased conductivity of the NRs from doping firstly leads to a reduction, then the passivation of surface traps with 3 dip cycles leads to a reduction below 1  $\Omega$ . The difference in  $R_s$  determined by EIS to the value from IV curve gradient is due to the differing potentials of testing. At low potential (0 V for EIS) the diodic character of the cell leads to increased resistance compared with IV values taken at the  $V_{oc}$ . This dual strategy leads to an accompanying drop in  $R^{z}_{ct}$ , promoting the transition of electrons across this boundary by reduced recombination, followed by their rapid transport from the surface.<sup>59</sup> The charge transfer and capacitive properties of the perovskite layer correspond closely to this trend, likely due to efficient charge extraction from the intrinsic material. If a large photocharge density builds up in the CsPbBr<sub>3</sub> layer without efficient transfer to the ETM, the resistance in the layer could increase from poor electron mobility and high scattering rate. This is likely the effect occurring in the 10 dips and Pristine samples.

The benefits of the dual enhancement can be seen clearly in the champion IV curve along with the external quantum efficiency plots, Figure 6A and B respectively. The samples show a three times increase in efficiency with Y doping, and a 9 times enhancement when TiO<sub>2</sub> coating are additionally employed, yielding PCE of 0.63, 2.10 and 5.83% for Pristine, Y doped and TiO<sub>2</sub> coated Y doped NRs respectively. This is reflected by dramatic increases in IPCE at 515 nm wavelength, leading to a doubling of value from ~15 to 30% with Y doping, and TiO<sub>2</sub> coating leading to nearly 70%. For the champion cell, at 400 nm wavelength the IPCE approaches 80% which is similar to the record holding ZnO based perovskite solar cell produced by Cao *et al.*<sup>14</sup> Photoluminescence spectroscopy measurements (Figure 6C) track the band edge emission of the perovskite. This confirms the passivation mechanism previously indicated by  $R_{ct}$ , with the 3 dip coating showing a dramatic fall in PL intensity, and so is the electron-hole recombination. Further coating thickness predictably reverses the trend, with greater surface roughness and cross linking seen in the SEM images in Figure 4.

The histograms of device performance for the 27 solar cells produced under identical conditions are displayed in Figure S12, with reasonable reproduction of efficiency. The majority fall from 2 to 4% efficiency. Growth by CBD inevitably leads to some variation in the NR length, and more reproducible methods, such as chemical vapour and microwave assisted deposition could be further investigated.<sup>60</sup> The other parameters of the 27 cells can be found in Figure S12B-D. Finally the efficiency was measured over time, showing no decline under initial value in dark storage under ambient conditions after 1000 hours, RH 50%, shown in Figure 6D. This indicates excellent stability, a weakness for most perovskite solar cells. The unusual feature is the dramatic increase in solar cell efficiency seen for the first 5 weeks of storage, which is as of yet unexplained. More subtle increases in solar cells built on ZnO NRs have been previously reported, and explained by perovskite relaxation improving the contact with the rods.<sup>61</sup> Alternately thermal aging of CsPbBr<sub>3</sub> solar cells at 45°C for 300 hours reportedly led to a significant improvement, attributed to a self doping mechanism at the perovskite crystal grain boundaries.<sup>62</sup> The root cause of this phenomenon will be assessed in future work.

The performance of the structure reported in this work compares very favourably with existing TiO<sub>2</sub> based CsPbBr<sub>3</sub> solar cells. As the first application of ZnO to CsPbBr<sub>3</sub> cells, the measured short circuit currents are high, surpassing 10 mA cm<sup>-2</sup> (Figure 5B), outstanding for a band gap of 2.3 eV. Thus far literature has been focused on modifying the CsPbBr<sub>3</sub> itself,<sup>63</sup> or the hole transport layer interface.<sup>64–66</sup> And so there is great potential for improvement by applying the strategies reported in this work. As for the wider application of these structures to other perovskites, this is the first time both coating and doping have been applied, leading to greater PCE than several MAPbI<sub>3</sub> cell structures.<sup>67,68</sup> However, it should be noted that in several

cases MAPbI<sub>3</sub> cells built on ZnO have achieved higher efficiencies between 10.45 and 12.77%, due to the more favourable band gap.<sup>69,70</sup> The dramatic enhancement seen in this work brings ZnO NRs closer than ever before to surpassing the performance of mesoporous TiO<sub>2</sub>.

# Conclusion

In summary, ZnO NRs have been shown to be a highly competitive alternative to mesoporous  $TiO_2$  as ETM for all-inorganic PSCs. From UV-Vis absorption and reflection data it is clear that the NRs are effective optical waveguides, delivering light to the CsPbBr<sub>3</sub>. Y doping of the NRs increased the efficiency of electron transfer from the perovskite by reducing overall series resistance of the solar cell. This optimisation strategy gave a three fold enhancement in the PCE of the solar cell. By then coating the ZnO with TiO<sub>2</sub>, surface traps were passivated, leading to reduced recombination and a further increase in photoconversion efficiency to a champion value of 5.83%. Due to the strengths of ZnO and the optimisation strategy, an improved  $J_{sc}$  of 10.5 mA/cm<sup>2</sup> for CsPbBr<sub>3</sub> was achieved. Finally, a novel back contact material was applied, multilayer graphite exfoliated by sonication, to the devices. This provides a step forward in further reducing the production cost of PSCs, leading them closer to commercialisation.

# **Supporting Information Available**:

Contains low magnification SEM of the perovskite / graphite junction, XPS survey scan used to determine valence band edges, optoelectronic material parameters, TEM surveys of exfoliated graphite, cross sectional SEMs of NRs, powder xrd of the varied length samples, top down SEM of these samples, full IV curves of length optimisation, binned NR diameter surveys, EDX maps of the TiO<sub>2</sub> coating, Nyquist plots of EIS with equivalent circuit and histograms of the optimised device performance.

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