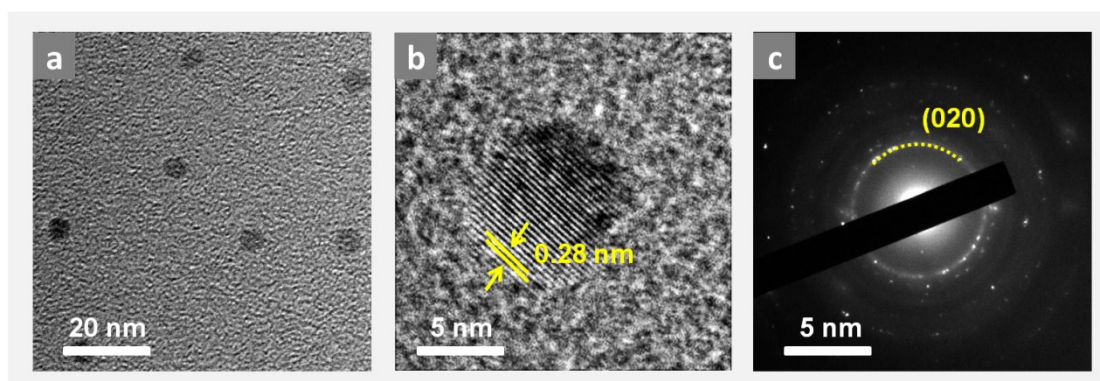


## Efficient Perovskite Solar Cells Enabled by Ions Modulated Grain Boundary Passivation with a Fill Factor Exceeding 84%

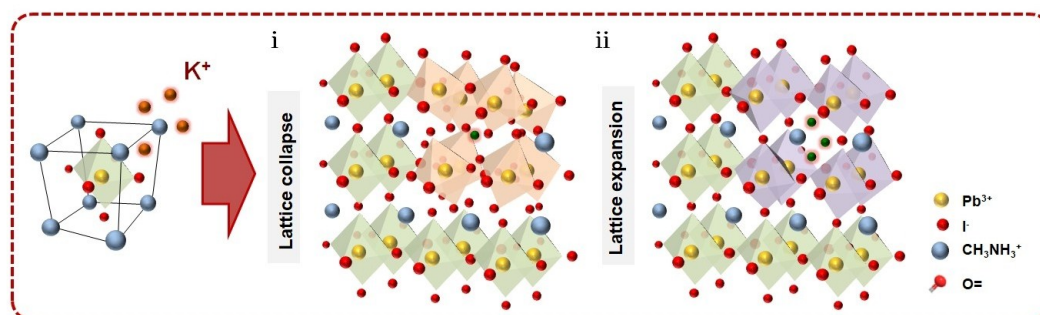
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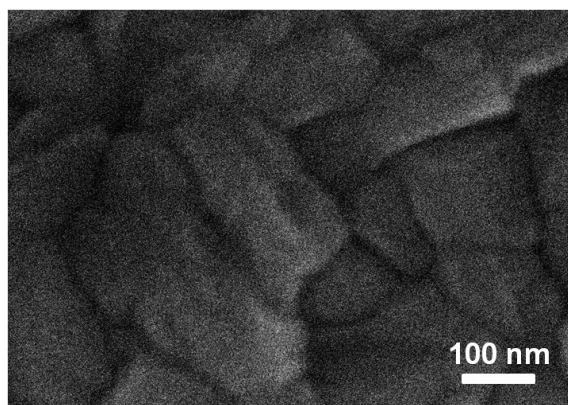
<sup>2</sup>Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping SE-58183, Sweden



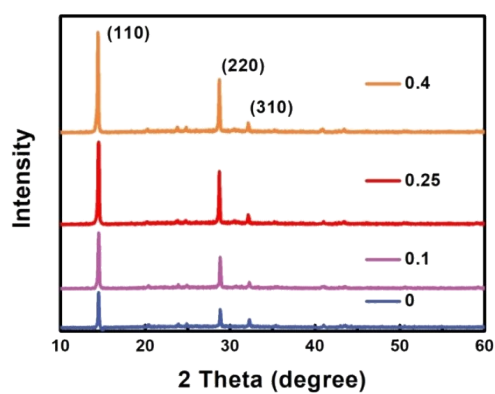
**Figure S1** a) The TEM image of CNDs at magnification of 20 nm; b) HRTEM image of CNDs@K at magnification of 5 nm, the crystal lattice of (002) plane is observed; c) Electron diffraction pattern of CNDs, diffraction circles from the (002) plane is observed.



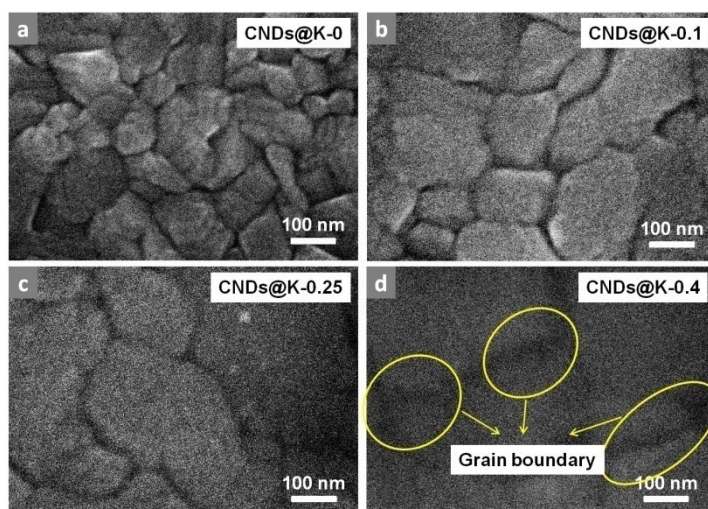
**Figure S2** Schematic diagram of the defects in K<sup>+</sup> doped perovskite lattice.



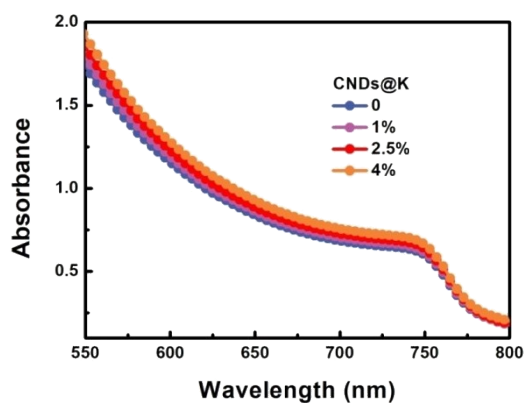
**Figure S3** Top-view SEM image of perovskite films with extra KI.



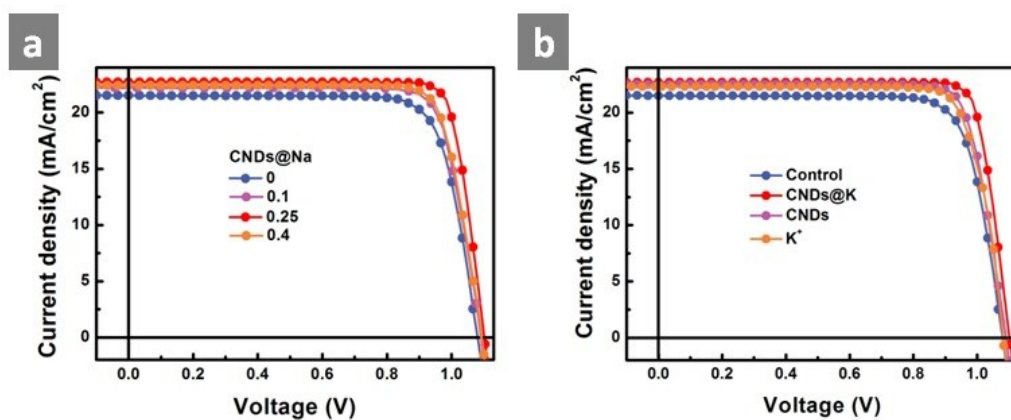
**Figure S4** XRD patterns of the perovskite films with various concentration of CNDs@K.



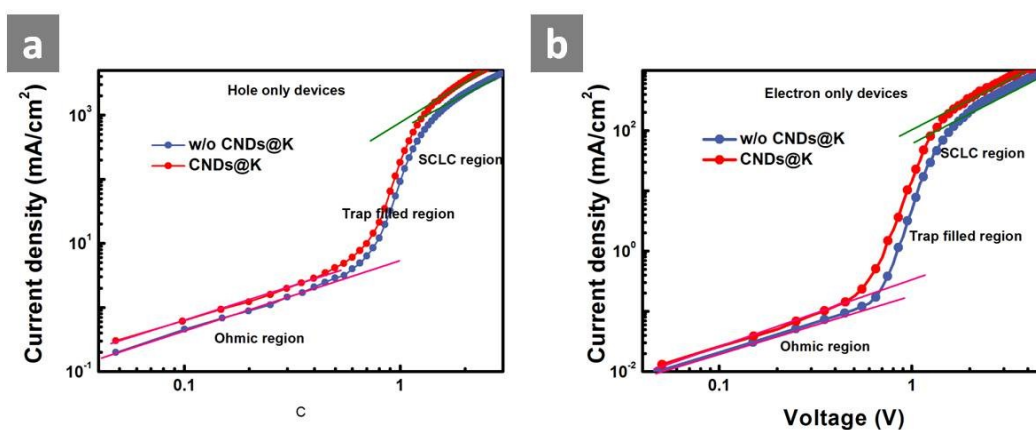
**Figure S5** Top-view SEM images of the perovskite films with CNDs@K concentration of (g) 0.1, (h) 0.25, and (i) 0.4 mg/mL, respectively.



**Figure S6** UV-vis absorption for the perovskite films with various concentrations of CNDs@K doping;



**Figure S7 a)**  $J$ - $V$  curves of perovskite devices with different amount of CNDs@K in the MAPbI<sub>3</sub> precursor solution; **b)**  $J$ - $V$  curves of perovskite devices with CNDs, K<sup>+</sup>, and CNDs@K in the MAPbI<sub>3</sub> precursor solution.



**Figure S8 a)** the  $J$ - $V$  curves of hole only devices without and with CNDs@K, **b)** the  $J$ - $V$  curves of the electron-only devices with and without CNDs@K; The electron only devices have the structure of ITO/PCBM/perovskite/PCBM/Bphen/Ag, and the hole only devices have the structure of ITO/PTAA/perovskite/ Spiro-OMeTAD/Ag.

**Table S1** The device parameters of devices without and with different additives.

			$V_{oc}$	$J_{sc}$	FF	PCE
Control	0	Best	1.08	21.51	78.51	18.25
		Average	1.08	21.48	76.29	17.76
CNDs@K	1	Best	1.09	22.19	80.57	19.49
		Average	1.09	22.09	79.11	19.14
	2.5	Best	1.10	22.69	84.07	21.01
		Average	1.10	22.60	82.93	20.51
	4	Best	1.09	22.41	81.01	19.84
		Average	1.09	22.33	80.41	19.58
KI	5	Best	1.08	22.32	80.85	19.51
		Average	1.08	22.24	79.11	19.01
CNDs	3	Best	1.09	22.51	81.60	20.03
		Average	1.09	22.42	80.29	19.61

## Experimental Section

### Materials

lead (II) iodide ( $PbI_2$ ), Methylamine iodide (MAI), bathocuproine (BCP), and PTAA were purchased from Xi'An P-OLED Co. (China). [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was purchased from American Dye Source Inc. Chlorobenzene (CB), N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were purchased from Aladdin. All of the chemical reagents are commercial available and used as received without further purification unless otherwise stated.

### Device Fabrication

For the device preparation, we follow the procedure reported elsewhere. All the preparation steps were conducted in dehumidified atmosphere ( $\sim 25^\circ C$ ,  $RH < 30\%$ ). The poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) hole transport layer was prepared by spin-coating a toluene solution containing PTAA with a concentration of  $5\text{ mg mL}^{-1}$  and 3 wt% F4TCNQ on the top of the pre-cleaned ITO-coated glass ( $2.0\text{ cm} \times 1.5\text{ cm}$ , sheet resistance:  $15\ \Omega\ \text{sq}^{-1}$ ) at the speed of 4000 rpm for 30 s. The PTAA-coated substrates were then baked at  $110^\circ C$  for 15 min in air. The  $MAPbI_3$  perovskite precursor solution was prepared by dissolving 461 mg  $PbI_2$  and 159 mg MAI in 78  $\mu\text{L}$  DMSO (molar ratio: 1:1:1) and 600  $\mu\text{L}$  DMF. The solution was stirred at room temperature for 12h. The CNDs, KI, and CNDs@K were directly added to the perovskite precursor solution for the fabrication of the corresponding device. The perovskite precursor solution was coated onto the PTAA:F4TCNQ/ITO substrate by an antisolvent extraction approach in air. Following prewetting of the substrates by spinning 50  $\mu\text{L}$  DMF at 4000 rpm for 8 s, the dissolved precursor solution was spin-coated on the PTAA layer at 4000 rpm for 25 seconds; 0.5 ml diethyl ether was slowly dripped on the rotating substrate 5 seconds after the start of the spin-

procedure. Subsequently, the transparent film was annealed at 60 °C for 1 min and 100 °C for 2 min to obtain a dense perovskite film. After cooling to room temperature, PCBM dissolved in anhydrous chlorobenzene with a concentration of 20 mg mL<sup>-1</sup> was coated onto the perovskite substrate by spin coating at 4000 rpm for 30 s. Bphen dissolved in absolute ethyl alcohol with a concentration of 0.7 mg mL<sup>-1</sup> was deposited on PCBM by spin coating at 5000 rpm for 30 s. Finally, the device was completed through the evaporation of Ag contact electrodes (100 nm) at a vacuum level of 10<sup>-5</sup> Pa through a shadow mask. The active area of this electrode was fixed at 0.04 cm<sup>2</sup>.

### **Device Characterization**

The current–voltage characteristics were recorded by a Keithley Model 2400 Source-Meter at a voltage scan rate of 0.1 V s<sup>-1</sup>. The measurements were conducted under a simulated AM 1.5G irradiation (100 mW cm<sup>-2</sup>) by a Newport solar simulator, and the light intensity was calibrated using a standard Si-solar cell. The steady-state PCE was measured by monitoring current with largest power output bias voltage and recorded the value of photocurrent (the steady-state  $J_{sc}$ ). External Quantum Efficiency (EQE) curves were measured using a QE measurement kit by focusing each monochromatic light onto the devices. X-ray diffractometer (XRD) measurements were performed using a glazing incidence X-ray diffractometer. Scanning electron microscopy (SEM) images were taken from a JSM-7600F hot field emission scanning electron microscopy. The steady state photoluminescence (PL) spectra of the perovskite films were measured by a fluorescence spectrophotometer with a standard light source. Time-resolved photoluminescence (TRPL) were recorded using a commercial fluorescence lifetime system.