

## Electronic Supplementary Information

### Rapid open-air deposition of uniform, nanoscale, functional coatings on high-aspect-ratio nanostructures

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#### **S1 – Experimental Methods**

*Nanorod synthesis:* All ZnO nanorods were synthesized on commercial ITO-glass substrates from Colorado Concepts LLC or Prazions Glas & Optik GmbH. ZnO nanorods that were coated with AP-SALD Cu<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> were synthesized using an electrochemical deposition method reported previously.<sup>[1]</sup> ZnO nanorods that were coated with AP-SALD ZnO and N-doped ZnO for ZnO nanorod-P3HT solar cells were synthesized using the following hydrothermal method. Sol-gel was prepared using zinc acetate dehydrate, 2-methoxyethanol, and ethanolamine (all from Sigma Aldrich) as the starting material, solvent and stabilizer, respectively. Initially, zinc acetate dehydrate was dissolved in the mixed solution of 2-methoxyethanol and ethanolamine (weight ratio of 96:4) with a concentration of 0.5 mol L<sup>-1</sup> at room temperature. The solution was spin-coated on ITO-glass substrates, followed by a heating process at 350 °C for 5 min. After cooling the films to room temperature, a second seed layer of ZnO was coated on top of the first one by repeating the last step. The hydrothermal growth was carried out in an aqueous solution of zinc nitrate and hexamethylene tetramine with equal molar concentrations of 0.05 M. The ZnO seed films were placed film-side down into this solution in a Teflon vessel, which was surrounded with

an oil bath at 95 °C. ZnO nanorods with lengths of approximately 300 nm were obtained after 60 min. Then the nanorod arrays were rinsed with deionized water, ultrasonically cleaned in ethanol, and dried with nitrogen gas. ZnO nanorods that were coated with AP-SALD ZnO, N-doped ZnO, and  $Zn_{1-x}Mg_xO$  for ZnO nanorod-PbSe colloidal quantum dot solar cells were synthesized using a slightly different hydrothermal method. A 100 nm thick seed layer of ZnO was grown by AP-SALD (using the conditions noted in Table S1) on the ITO-glass substrates. The coated substrates were suspended facing downwards in a solution composed of zinc nitrate and hexamethylene tetramine with equal molar concentrations of 0.025 M. The solution was in a Teflon flask, which was closed and put into an oven pre-heated at 90 °C. The nanorods were grown for 37 min, producing  $140 \pm 30$  nm long nanorods (determined from cross-sectional SEM images of devices). After growth, the nanorods were sonicated for 10 s in deionized water and dried with compressed air.

*AP-SALD depositions:* The experimental conditions used to deposit the coatings are summarized in Table S1. The first and second set of conditions listed in Table 1 for N-doped ZnO correspond to those used to coat the ZnO nanorods for use in the colloidal quantum dot solar cells and hybrid solar cells respectively.

**Table S1.** Atmospheric-pressure spatial atomic layer deposition (AP-SALD) conditions used to deposit the coatings discussed in this work.

Material deposited	Precursors	Speed of substrate oscillation (mm s <sup>-1</sup> )	Metal precursor bubbling rate (ml min <sup>-1</sup> )	Oxidizing precursor bubbling rate (ml min <sup>-1</sup> )	Carrier gas flow rate for metal/oxidizing precursors (ml min <sup>-1</sup> )	Shielding gas (nitrogen) flow rate (ml min <sup>-1</sup> )
Al <sub>2</sub> O <sub>3</sub>	Trimethylaluminium, Water	2 25	10 25	25 50	100/100 150/150	3000 750
ZnO	Diethylzinc, Water	50	15	40	250/250	750
Zn <sub>1-x</sub> Mg <sub>x</sub> O	Diethyl zinc (DEZ), Mg(CpEt) <sub>2</sub> <sup>a)</sup> , Water	50	5 (DEZ), 500 (Mg(CpEt) <sub>2</sub> )	100	200/200	500
N-doped ZnO	Diethylzinc, 30% Ammonia in water	50 50	25 25	100 50	125/200 150/150	600 750
Cu <sub>2</sub> O	Cupraselect <sup>b)</sup> , Water	10 50	400 30	50 100	100/100 150 /100	2500 2000

a) bis(ethylcyclopentadienyl)magnesium; b) heated to 65 °C

*Material characterization:* SEM imaging and EDX analysis was performed using a LEO VP-1530 field-emission scanning electron microscope equipped with an Oxford Instruments EDX detector. TEM imaging of the Al<sub>2</sub>O<sub>3</sub> coatings was performed with a Philips CM30 TEM operating at 300 kV in bright field conditions. TEM imaging of the Cu<sub>2</sub>O coatings was performed with a FEI Tecnai F20 TEM operating at 200 kV. TEM images of the ZnO and N-doped ZnO coatings were taken along (or close to) the ZnO <11-20> zone axis using a FEI Tecnai F20 microscope operated at 200 kV. Structural and crystallographic characterization (not shown here) was also performed on a Jeol 4000EX operated at 400 kV.

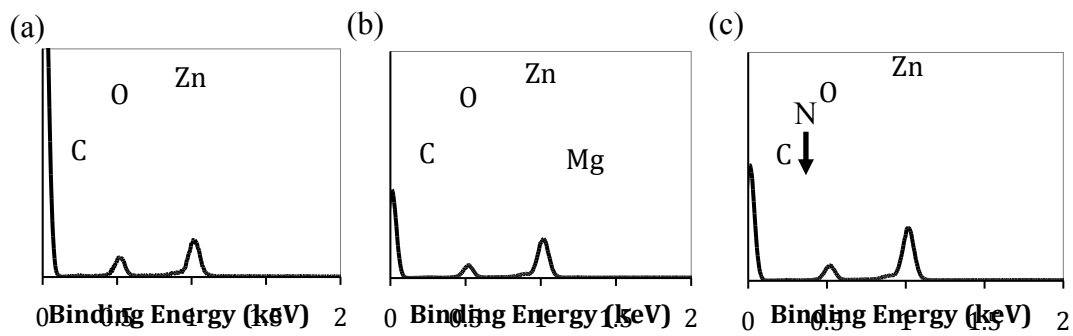
Photoluminescence spectra were measured at room temperature using an ACCENT RPM 2000 system with a Nd:YAG laser (266 nm wavelength, 4.5 mW power).

*PbSe colloidal quantum dot device fabrication:* After coating, the ZnO nanorods were annealed at 350 °C for 60 min. The PbSe quantum dots were synthesized using a procedure reported previously.<sup>[2]</sup> Nine layers of the PbSe quantum dots were deposited on the nanorod arrays. The spinning conditions for each layer involved 30 s at 0 rpm for ligand exchange/washing, followed by 7 s at 1500 rpm. The order of deposition was the same as that reported previously,<sup>[2]</sup> except that 3-mercaptopropionic acid (MPA) was used here as the cross-linker. The concentration was 1.7  $\mu\text{L}$  MPA in 1 mL methanol (0.17 vol.%). A top electrode ( $\text{MoO}_3/\text{Au}$ ) was deposited by thermal evaporation.

*P3HT device fabrication:* The hydrothermally-grown ZnO nanorods were coated with 30 AP-SALD oscillations (approximately 10 nm) of ZnO or N-doped ZnO. Poly(3-hexylthiophene) (P3HT) was dissolved in chlorobenzene to form 5 mg  $\text{ml}^{-1}$  and 30 mg  $\text{ml}^{-1}$  solutions. The nanorod arrays were sonicated in the 5 mg  $\text{ml}^{-1}$  P3HT for 3 min then coated immediately with the 30 mg  $\text{ml}^{-1}$  P3HT using a spin coater (800 rpm for 1 min), resulting in homogenous filling and complete coverage of the ZnO nanorod array. The P3HT film was then dried at room temperature. Polystyrene sulfonate (PEDOT:PSS) was spin-cast on top in air to act as an electron-blocking layer and a silver electrode was thermally evaporated on top.

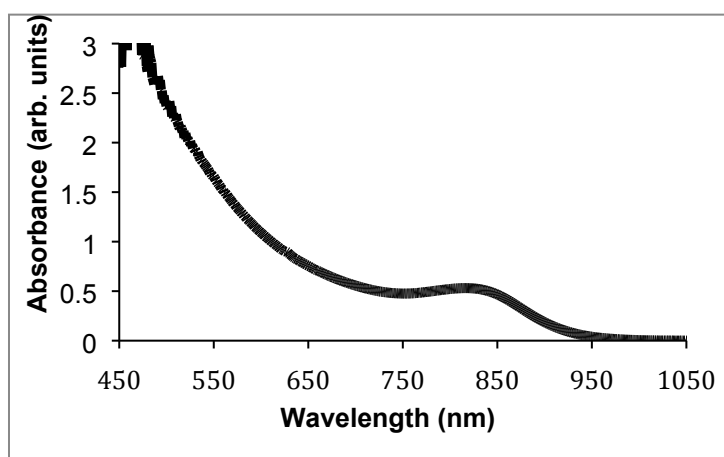
*Device characterization:* Current density–voltage measurements were taken using a Keithley 2636A source-measure unit under simulated AM1.5G solar illumination provided by an Oriel 92250A solar simulator, at an intensity equivalent to 100  $\text{mW cm}^{-2}$  after correcting for spectral mismatch. External quantum efficiencies were measured using a tungsten light source, Oriel Cornerstone 260 monochromator, and reference diode.

## S2 – Energy Dispersive X-Ray Spectroscopy



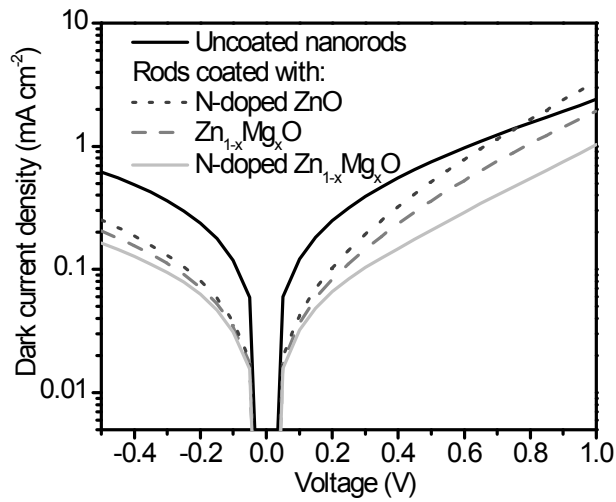
The figure shows energy dispersive X-ray spectra of ZnO nanorod arrays (a) uncoated, (b) coated with  $Zn_{1-x}Mg_xO$ , and (c) coated with nitrogen-doped ZnO. The peak in (b) indicates the presence of Mg. The broad O peak in (c) covers the expected emission corresponding to the presence of N.

### S3 – Band-gap measurement of PbSe quantum dots



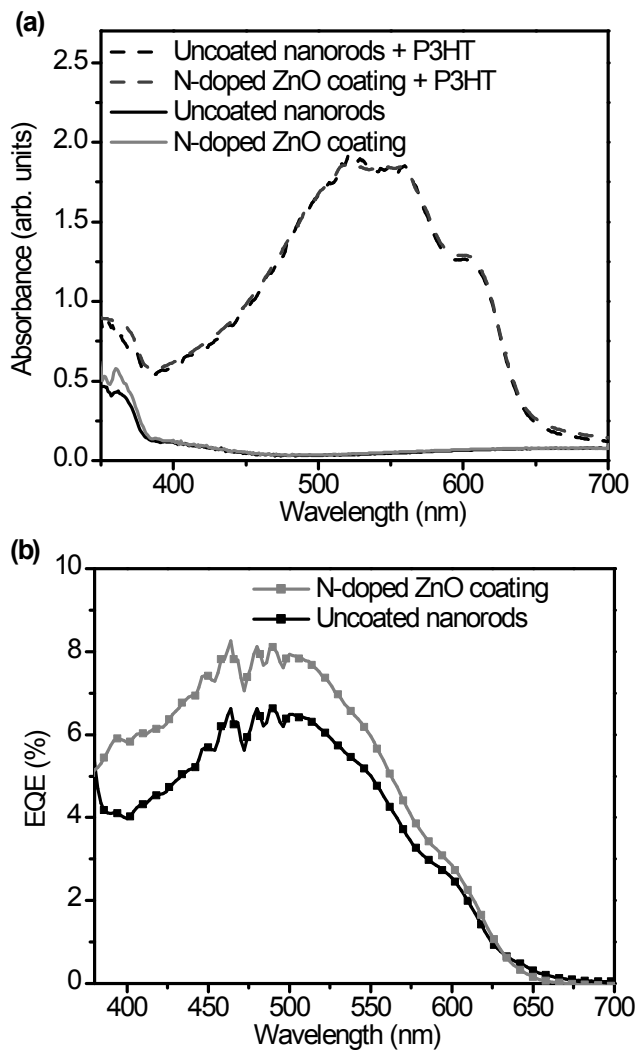
Absorbance measurement of PbSe quantum dots with a bandgap of approximately 1.51 eV.

#### S4 – Dark current density measurements of colloidal quantum dot solar cells



The figure shows dark current density-voltage measurements of the ZnO nanorod-PbSe colloidal quantum dot solar cells with and without various AP-SALD coatings to engineer the charge-separating interface. The reduction in recombination current achieved with the AP-SALD coatings is evident in the log-linear plot. All devices with AP-SALD coatings at the interface demonstrated significantly reduced dark currents compared to the device with uncoated nanorods.

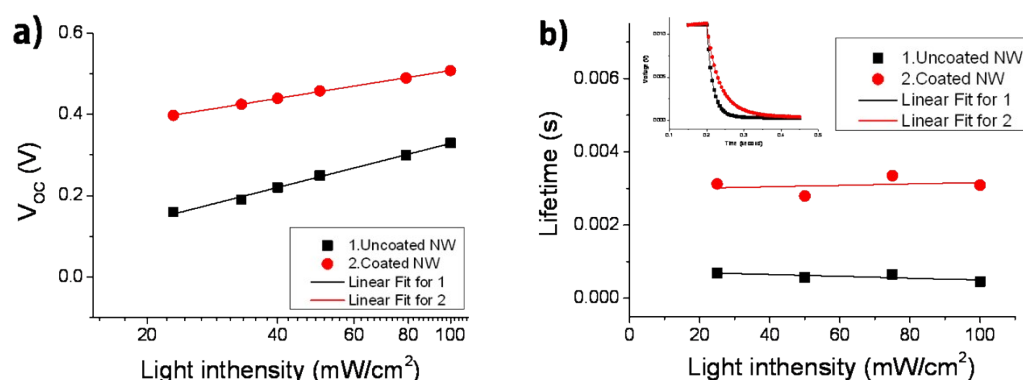
## S5 – Characterization of ZnO nanorod-P3HT solar cells



Part (a) of the figure shows the absorption spectra of a pristine ZnO nanorod array, a ZnO array coated with N-doped ZnO, and both types of array infiltrated with P3HT. The absorption spectra were identical for the coated and uncoated nanorod samples. Part (b) of the figure shows external quantum efficiency (EQE) measurements for the ZnO nanorod-P3HT devices with pristine ZnO nanorods and nanorods coated with N-doped ZnO. The EQE of the coated device was seen to be slightly higher, consistent with the larger short-circuit current observed in Figure 5c of the main text. Notably, the EQE enhancement was highest for shorter wavelengths, which would be absorbed in the P3HT close to the nanorod interface. This is



consistent with a reduction in the recombination of holes from the P3HT with electrons from the nanorods with the introduction of the coating.



This figure displays measurements of the (a) open-circuit voltage ( $V_{oc}$ ) and (b) photovoltage decay time as a function of light intensity for ZnO nanorod-P3HT solar cells with and without a N-doped ZnO nanorod coating. The open-circuit voltage of the devices shows a logarithmic dependence on light intensity as expected. The slope of the device with coated nanorods was smaller than that of the uncoated device. This suggests less recombination may occur in the coated devices, consistent with the larger open-circuit voltage observed. The photovoltage decay results in (b) provide strong evidence for the enhanced charge carrier lifetime in the coated device. The photovoltage decay measurements were carried out by illuminating the cells with a white light bias with increasing light intensity. At the same time, a green (525 nm) LED pulse (generated by a Hewlett-Packard 8116A pulse/function generator) illuminated the devices to generate charge carriers. The decay of the photovoltage generated by the green LED was recorded using an Agilent DSO6052A digitalizing oscilloscope (input impedance 1  $\text{M}\Omega$ ) and fit with an exponential relation to determine the carrier lifetime.

## References

- [1] K.P. Musselman, A. Wisnet, D.C. Iza, H.C. Hesse, C. Scheu, J.L. MacManus-Driscoll, L. Schmidt-Mende, *Adv. Mater.*, 2010, **22**, E254.
- [2] R.L.Z. Hoye, B. Ehrler, M.L. Böhm, D. Muñoz - Rojas, R.M. Altamimi, A.Y. Alyamani, Y. Vaynzof, A. Sadhanala, G. Ercolano, N.C. Greenham, R.H. Friend, J.L. MacManus-Driscoll, *Adv. Energy Mater.*, 2014, **4**, 1301544.