

Supporting Information

High Reduction of Interfacial Recombination in Colloidal Quantum Dot Solar Cells by Metal Oxide Surface Passivation

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Optimization of annealing temperature T1

The effect of annealing temperature T1 (as shown in Figure 1 in main text) for ZnO compact layer on the ZnO-NWs morphologies was investigated. As shown in Figure S1, ZnO-NW arrays were obtained when the compact seed layer was annealed at temperatures over 150 °C. In contrast, ZnO nanofibers were produced when the seed layer was annealed at 100 °C, which could be due to the the poor crystallinity of ZnO seeds obtained at relatively low annealing temperature. When T1 was 150 °C, uniform ZnO-NW arrays were obtained with diameter in the range of 30 - 40 nm. The density of arrays (the number of arrays per μm^2) was approximately 130 wires/ μm^2 , suggesting their high surface area and QD loading ability. In the case of 200 °C and 250 °C, the average diameter of ZnO-NW arrays was slightly increased to 40 - 50 nm with bonded NWs, which would likely ruin the reproducibility of device performances.

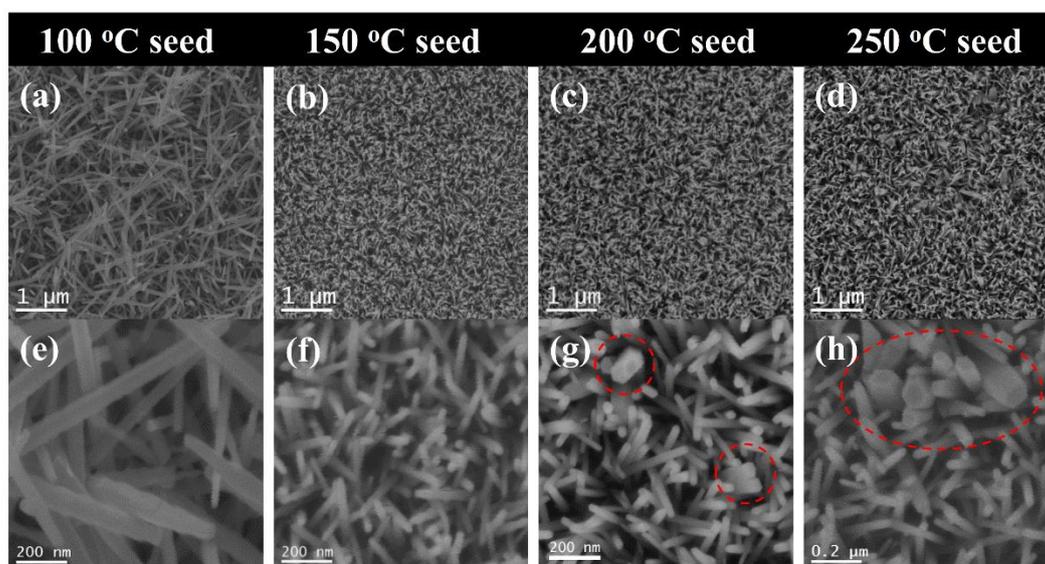


Fig. S1 SEM images of ZnO-NWs grown on compact ZnO seed layers, which were pre-annealed at various temperatures for 10 min: (a, e): 100 °C, (b, f): 150 °C, (c, g): 200 °C, and (d, h): 250 °C. (a-d) and (e-h) are low and high magnification SEM images, respectively. The marked areas in (g, h) show the poor uniformity of ZnO-NWs with bonded nanowires, which were grown on high temperature annealed (200 °C, 250 °C) seed layers.

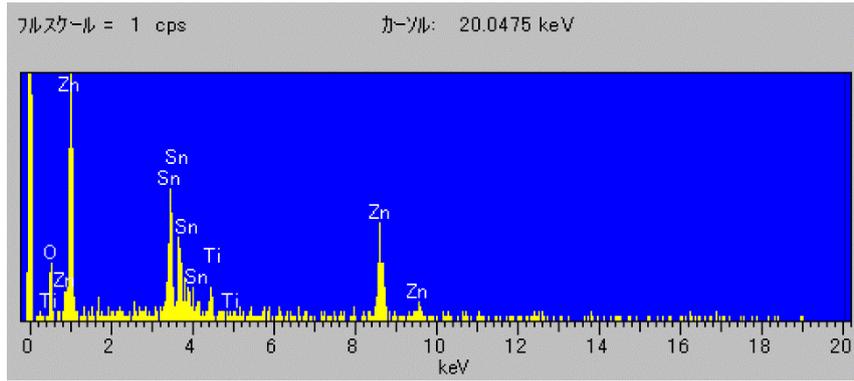


Fig. S2 Energy Dispersive X-ray Spectroscopy (EDX) image of ZnO@TiO₂-NW arrays prepared by dipping ZnO-NWs in a 5 mM (NH₄)₂TiF₆ and H₃BO₃ aqueous solution.

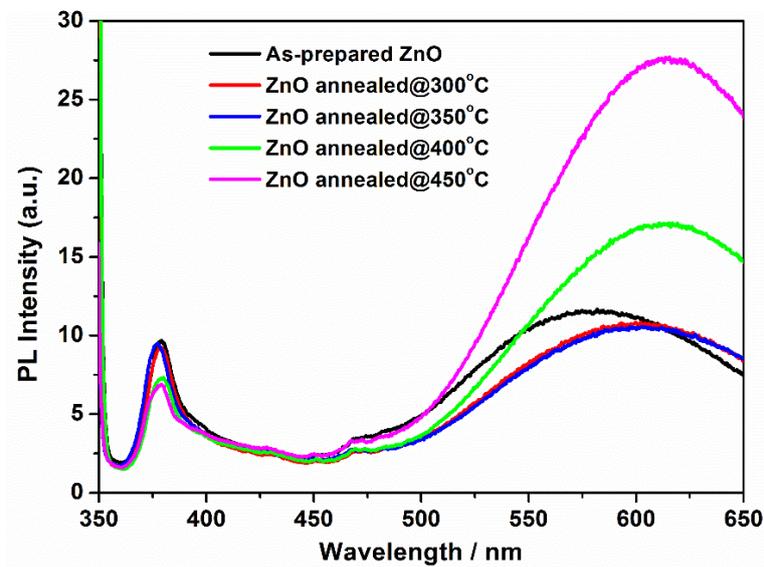


Fig. S3 Room temperature PL spectra of as-prepared ZnO-NWs and the samples annealed at various temperatures in air for 30 min (excitation wavelength: 340 nm).

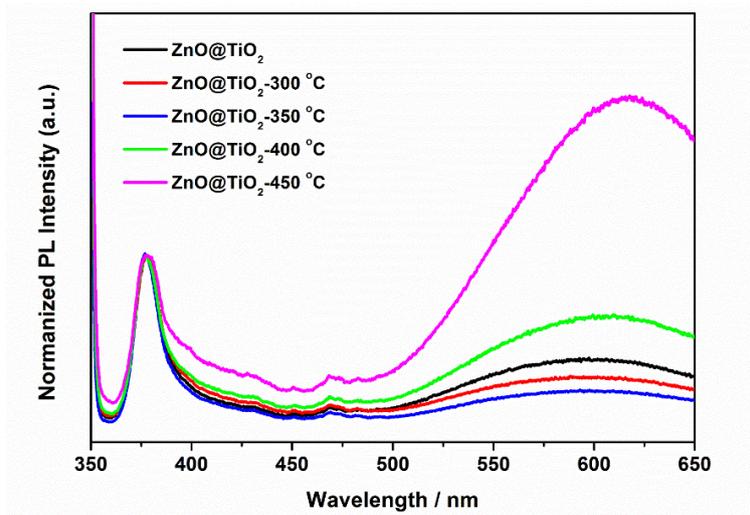


Fig. S4 Room temperature PL spectra of as-prepared ZnO@TiO₂-NWs and the samples annealed at various temperatures in air for 30 min (excitation wavelength: 340 nm).

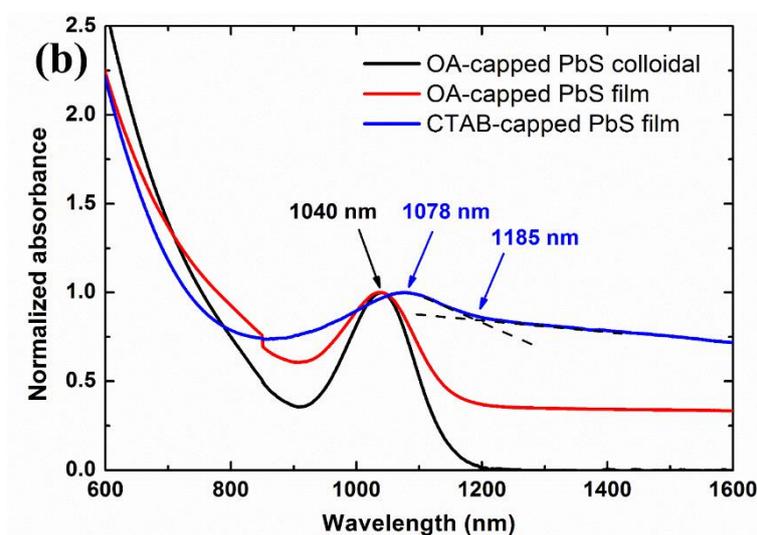
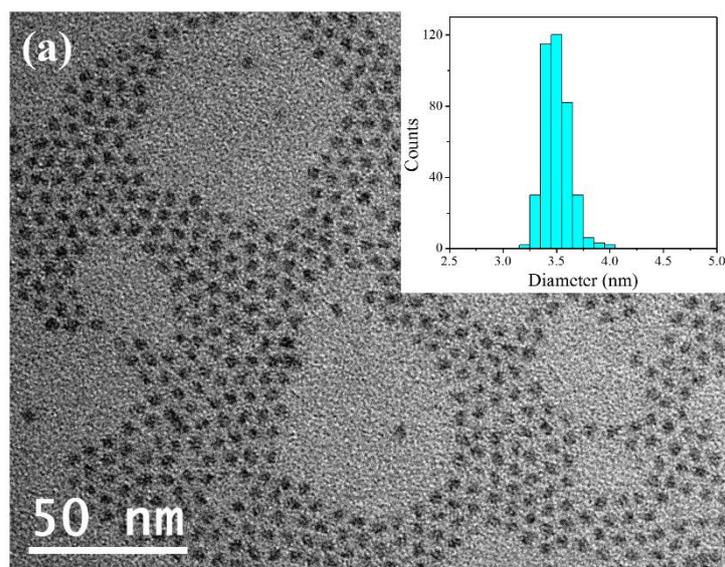


Fig. S5 (a) TEM image and size distribution of OA-capped PbS QDs. (b) UV-vis-NIR absorption spectra of OA-capped PbS QDs colloidal, OA-capped PbS film, and CTAB-capped PbS film, respectively. The absorption peaks of OA or CTAB-capped PbS films are 1040 nm and 1078 nm, respectively. The absorption onset of the CTAB-capped PbS film is 1185 nm.

Energy Level Determination

Photoelectron yield spectroscopy (PYS) measurements were taken to determine the valence band maximum (E_v) with respect to vacuum level of ZnO and PbS films, respectively. The basic principle is illustrated in Fig. S6a. All samples were illuminated by a UV light with maximum incident photon energy of 9 eV. When the incident light energy is larger than the ionization potential (IP) (i.e. E_v of semiconductors) of samples, photoelectrons would escape the sample surface and to be collected by a counter. The photoelectron yield is derived by dividing the number of collected electrons by the number of incident photons. The ionization potential of samples can be determined by the intersection of the linear portion of the

photoelectron yield spectrum and the baseline. Fig. S6 b, c show the photoelectron yield spectra of ZnO@TiO₂-NWs and PbS film, respectively. It can be seen that the ionization potential of ZnO@TiO₂-NWs was determined as 7.6 eV; that is, the valance band maximum (E_v) is -7.6 eV with respect to the vacuum level. Similarly, the valance band maximum of PbS film was determined as -5.2 eV (Fig. S6c).

The conduction band minimum (E_c) of ZnO@TiO₂-NWs and PbS films are calculated by $E_c = E_v + E_g$, where E_g is the band gap values obtained from their UV-vis-NIR absorption onset. As shown in Fig. S5b and Fig. S7, the optical absorption onset of PbS and ZnO films are 1185 nm and 378 nm, respectively. The band gap of ZnO@TiO₂-NWs and PbS film are estimated as 3.3 eV and 1.0 eV, respectively. Therefore, the E_c values of ZnO@TiO₂-NWs and PbS film are calculated as -4.3 eV and -4.2 eV, respectively, as shown in Fig. 5a in the main text.

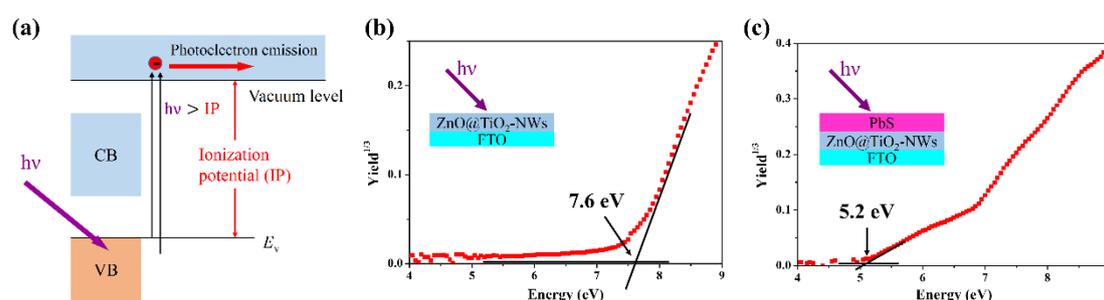


Fig. S6 (a) Schematic principle of the photoelectron yield spectroscopy. (b, c) Photoelectron yield spectra of ZnO@TiO₂-NWs and PbS films, respectively. The threshold energy for the photoelectron emission was estimated on the basis of the third root of the photoelectron yield plotted against the incident photon energy.

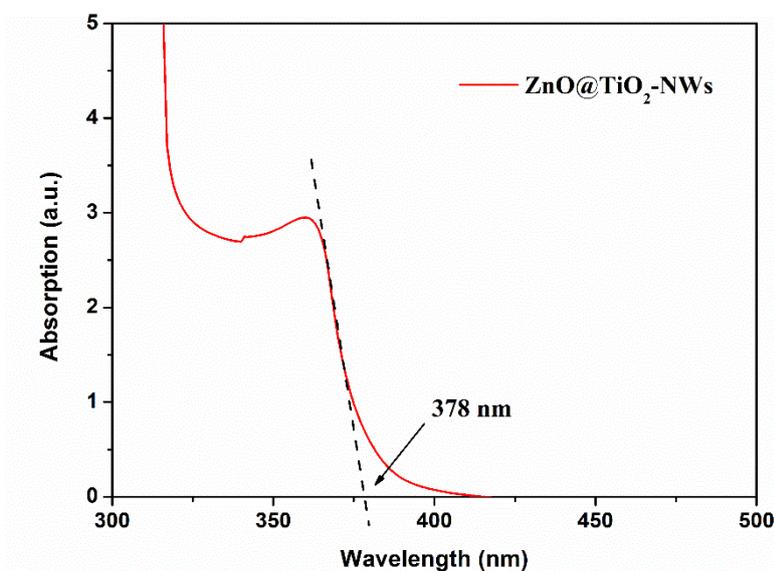


Fig. S7 UV-vis absorption spectrum of ZnO@TiO₂-NW arrays, showing the absorption onset of 378 nm.

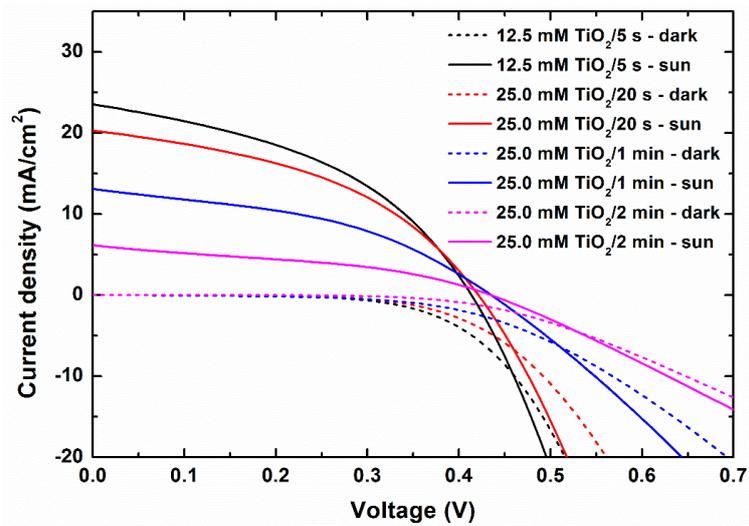


Fig. S8 J - V curves of ZnO@TiO₂/PbS CQDSCs based on ZnO-NWs treated by TiO₂ precursors at 10 °C with different concentrations and treatment times.

Table S1 Device parameters of ZnO@TiO₂/PbS CQDSCs based on ZnO-NWs treated by TiO₂ precursors at 10 °C with different concentrations and treatment times.

TiO ₂ precursor conc.	Treatment time	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
12.5 mM	5 s	23.5	0.41	0.43	4.1
25.0 mM	20 s	20.3	0.42	0.43	3.7
25.0 mM	1 min	13.1	0.44	0.42	2.4
25.0 mM	2 min	6.16	0.44	0.39	1.0

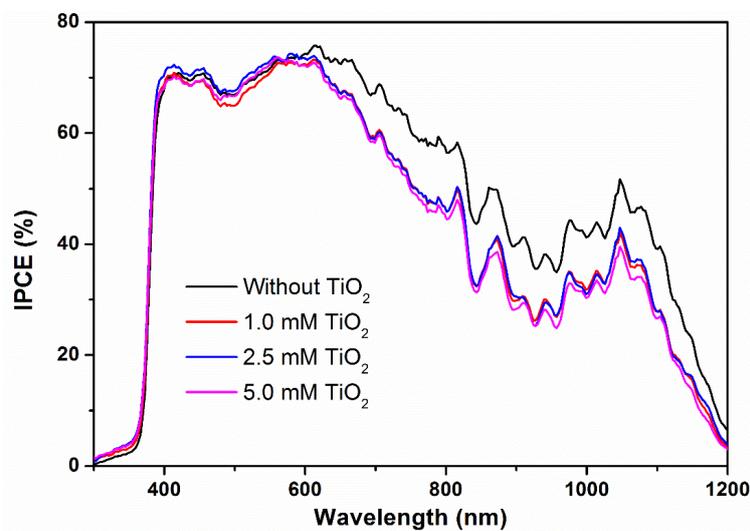


Fig. S9 IPCE spectra of PbS CQDSCs based on ZnO-NW arrays with and without TiO₂ treatment.

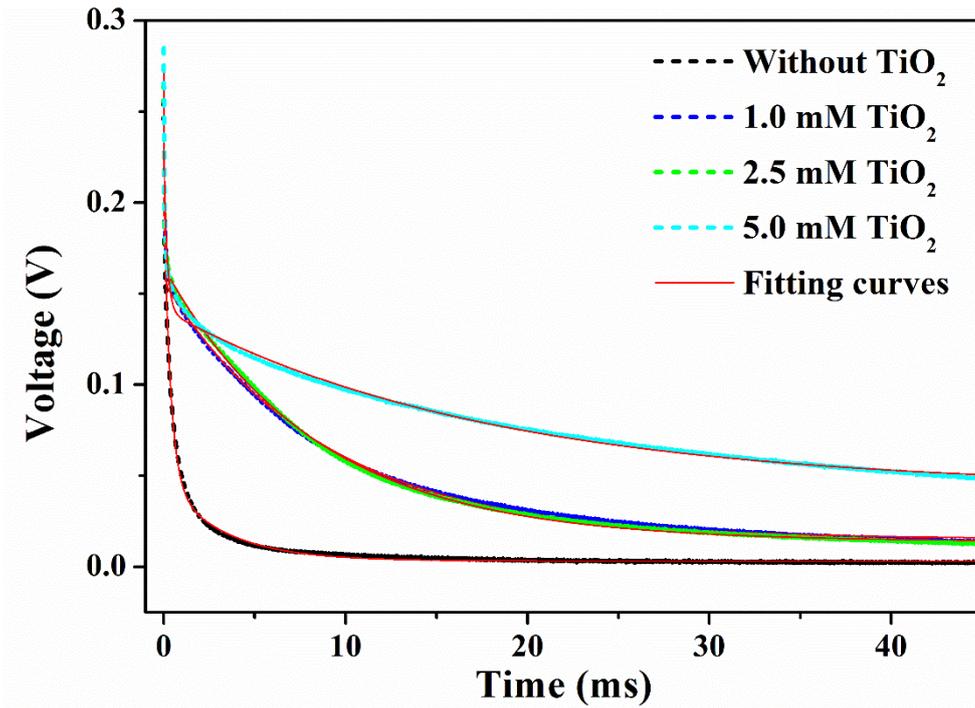


Fig. S10 Normalized transient photovoltage decay curves and the corresponding fitted curves of PbS CQDSCs based on ZnO-NWs (with and without the TiO₂ treatment).

Deduction of the Effective Carrier Lifetime

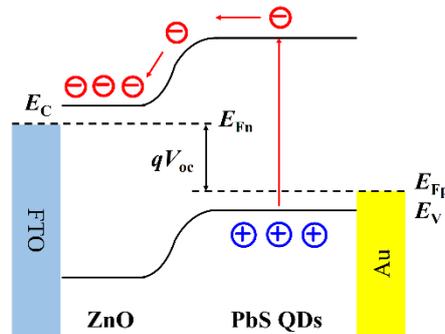


Fig. S11 Illustration of the energy level alignment and junction potential in ZnO/PbS p-n junction solar cells under open circuit condition.

Fig. S11 illustrates the energy level alignment of FTO/ZnO/PbS/Au p-n junction solar cells under open circuit condition. The open-circuit voltage (V_{oc}) is determined by the following equation:

$$qV_{oc} = E_{Fn}(ZnO) - E_{Fp}(PbS) \quad (1)$$

where q is the elementary charge; E_{Fn} and E_{Fp} are the quasi-Fermi levels of n-type ZnO and p-type PbS, respectively. The position of E_{Fn} and E_{Fp} can be easily determined from equation (2, 3):

$$E_{Fn}(ZnO) = E_c + kT \ln(n/N_c) \quad (2)$$

$$E_{Fp}(PbS) = E_v - kT \ln(p/N_v) \quad (3)$$

where k is the Boltzmann constant, T is the temperature, E_c and E_v are the conduction band minimum of ZnO and the valance band maximum of PbS, respectively; n is free electron density in ZnO; p is free hole density in PbS; N_c and N_v are the effective density of states of ZnO and PbS, respectively. According to equation (1-3), the derivative of voltage with respect to time, dV_{oc}/dt , can be calculated by equation (4), where τ_n and τ_p are electron and hole lifetimes in ZnO and PbS, respectively. For the sake of simplicity, we combined both the electron and hole lifetimes, and defined the effective carrier lifetime (τ_{eff}) as shown in equation (5).

$$\left(\frac{dV_{oc}}{dt}\right) = -(kT/q)[(dn/dt)/n + (dp/dt)/p] = -(kT/q)(1/\tau_n + 1/\tau_p) \quad (4)$$

$$\tau_{eff} = 1/(\tau_n^{-1} + \tau_p^{-1}) = -(kT/q)/\left(\frac{dV_{oc}}{dt}\right) \quad (5)$$

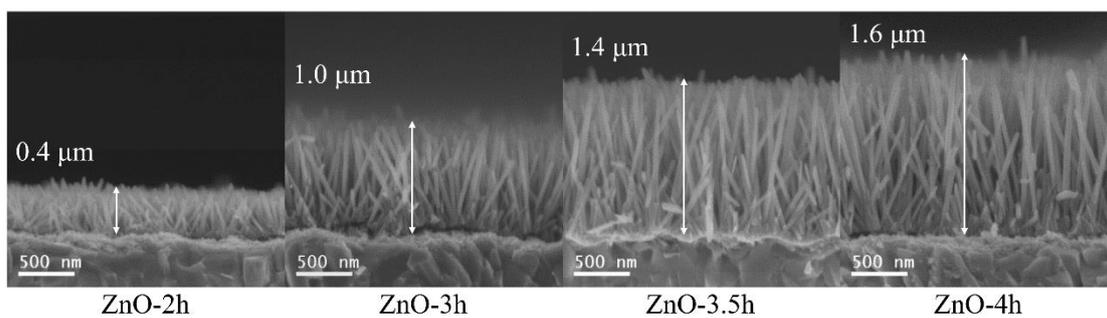


Fig. S12 Cross-section SEM images of ZnO-NW arrays grown on FTO-coated glasses, with various growth times and NW length.

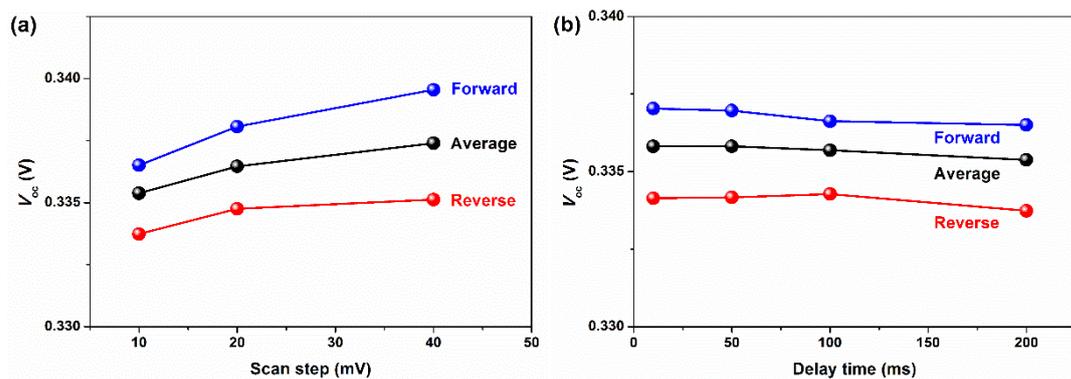


Fig. S13 (a) Relationship between V_{oc} and voltage scan step obtained from J - V curves of ZnO@TiO₂/PbS cells measured by forward and reverse scans with delay time of 200 ms. (b) Relationship between V_{oc} and decay time obtained from J - V curves of ZnO@TiO₂/PbS cells measured by forward and reverse scans with 10 mV voltage steps.