Supporting Information

Finely Interpenetrating Bulk Heterojunction Structure for Lead Sulfide Colloidal Quantum Dot Solar Cells by Convective Assembly

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**Experimental section:**

**Synthesis of Colloidal Quantum Dots:**

All operations were performed under a nitrogen atmosphere by using standard air-free Schlenk line techniques. A solution of 223 mg of PbO (1 mmol), 0.7 g of oleic acid (2.5 mmol), and 20 g of ODE (1-Octadecene) were degassed at 100 °C in a 100 mL three-neck flask for 1 h under vacuum. The solution was then heated for an additional 1 h to 150 °C under nitrogen. After cooling the solution down to 80 °C, 0.5 mmol of (TMS)$_2$S dissolved in 5 mL ODE was rapidly injected into the prepared solution. The CQDs were grown for 10 min and the reaction was rapidly quenched by placing the flask in a water bath at RT. After the injection of 8 mL of anhydrous hexane, purification procedures were carried out in hexane/isopropyl alcohol and hexane/acetone by precipitating the solution twice and once consecutively, prior to the storage of the with solid form in a nitrogen-filled glove box.

**Preparation of ZnO NW arrays:**

Seed layers: Sol-gel ZnO seed layers were prepared by thermal hydrolysis of zinc acetate precursor on ITO substrate. The patterned ITO glasses were sequentially cleaned in deionized water, isopropanol and acetone in an ultrasonic apparatus, prior to UV-ozone treatment for 30 min. The precursor was prepared by dissolving 220 mg of ZnAc$_2$·2H$_2$O in 2 mL 2-methoxyethanol and 61 μL ethanolamine and stirring for 5 min. The solution was filtered through a 0.22 mm PVDF syringe filter and deposited on pre-cleaned ITO glass at 4000 rpm for 30s, prior to annealing at 150 °C for 20 min under a relative humidity of 50-60%. ZnO nanoparticles were synthesized according to the literature. Zinc acetate dehydrate (2.95 g) was dissolved in 125 mL of methanol at 60 °C. Potassium hydroxide (1.48 g) was dissolved in 65 mL of methanol. Potassium hydroxide solution was slowly added to the zinc acetate solution and the solution was kept stirring at 63 °C for 3 h. Synthesized ZnO nanocrystals were extracted by from their mother solution via centrifugation and washed twice by methanol, prior to the repetition of the centrifugation procedure. Finally, 10 mL of chloroform and 10 mL of methanol were added to the precipitates and the solution
was filtered through a 0.45 µm filter. ZnO NCs solution was then spin-coated on ITO substrate at 2500 rpm for 30s without any sequential annealing process.

Growth of ZnO NWs: After the preparation of ZnO seed layers, ZnO nanowires were then grown by immersing the substrates into a growth solution of equal volumes of zinc nitrate hexahydrate (0.05 M) and hexamethylenetetramine (0.05 M) in DI water, for 30 min at 90 °C. As-grown ZnO nanowire arrays were thoroughly rinsed with DI water and annealed at 120 °C for 5 min to remove residual water.

ABA modification:

Self-assembled monolayers were prepared by soaking ZnO substrates into ABA methanol solution with a concentration of 0.01 wt%, for 1 min. The substrates were then dipped into pure MeOH followed by annealing at 120 °C for 10 min. All of the processes were conducted under the nitrogen atmosphere.

Fabrication of CQD OBHJ Solar Cells:

Spin coating: The CQD layers were stacked through the layer-by-layer (LbL) deposition method. PbS-TBAI films were prepared by spinning coating PbS CQDs from 40 mg mL\(^{-1}\) hexane solution at 2500 rpm. The ligand exchange was carried out by soaking the as-prepared film in 10 mg mL\(^{-1}\) TBAI methanol solution for 30s, and then rising with pure methanol followed through dropwise washing with acetonitrile on top of the surface of PbS layers to remove the excess of TBAI and oleic acid. This procedure was repeated for 5 times to achieve the desired thickness of 250 nm. After the deposition of PbS-TBAI layers, a PbS-EDT layer was immediately deposited on top of PbS-TBAI layers. 20 mg mL\(^{-1}\) PbS was coated at 2500 rpm for 15 s followed by the ligand exchanging by EDT solution (0.04 vol% in acetonitrile) for 30s and acetonitrile rinsing for twice. This procedure was repeated twice to get a thickness of 40 nm.

Convective assembly: The coating process starts from injecting droplet of CQDs solution between the deposition blade and substrate. Driven by the evaporative flows as a result of the coffee ring effect, the CQDs flow to the contact line of the meniscus
along with the receding of substrate. After the gentle evaporation of solvent, a thin film can be formed where the capillary bridges can force the dense packing of CQDs and the close contact between CQD and substrate. In order to achieve morphological controllability of CQD films for the construction of solar cells through convective assembly, the detailed deposition conditions were investigated based on the microscopic model proposed by Maël Le Berre et al.\textsuperscript{1} Through optimization of solvent, receding speed and solution concentration, CQD films with extremely large-area homogeneity were obtained as shown in Figure S6. For the optimal deposition conditions, hexane was used as CQD solvent with a concentration of 80 mg/ml. 10 uL of the CQDs solution was placed between the glass blade and ITO substrate. The glass and substrate keep an angle of 45° and a distance of over 1 μm. A stepper motor was used to recede the substrate with a speed of 1 mm s\textsuperscript{-1}. The whole deposition process was conducted in a fume hood at room temperature under ambient atmosphere. After film deposition, the ligand exchange process was carried out in the fume hood. This procedure was repeated for 10 times to achieve the desired thickness. The prepared devices were then stored under dry air overnight for further oxidation. Before the evaporation of metal electrode, the CQD devices were annealed at 80 °C for 30 min in a fume hood under ambient atmosphere. Finally, a 100 nm Au layer (0.5 Ås\textsuperscript{-1}) was evaporated through thermal evaporation under high vacuum lower than 1 × 10\textsuperscript{-5} mbar through a shadow mask.

Measurements:

Current density-voltage (J–V) characteristics of the devices were measured under ambient air using a programmable Keithley 2401 source meter under a simulated AM 1.5G solar irradiation of 100 mWcm\textsuperscript{-2} (Otento-sun III). A metal mask was used for defining the active area of 0.05 cm\textsuperscript{2}. The XRD patterns were measured by Rigaku, Smartlab. As for the cross-section TEM and SEM images, the thin film samples were prepared by FIB after carbon coating. The TEM and EDX were operated with JEOL JEM-2010FEF at 200 kV. SEM images were captured through FESEM, Hitachi SU-6600. Electrochemical impendence spectra and IMVS/IMPS profiling was carried
out using Zahner IM6 electrochemical workstation while applying a bias of under open circuit with a frequency between 0.25 MHz and 0.05 Hz under varying intensities of light illumination with a 500 nm LED. The IMPS represents the frequency where each imaginary part reaches its minimum value. The XPS spectra were obtained using a Kratos AXIS Ultra DLD ultrahigh vacuum photoemission spectroscopy system, with an Al Ka radiation source. UPS measurements were performed using an Omicron Nanotechnology system with a base pressure of 2 x 10^{-10} Torr. The light-dependent open circuit voltages were measured under a 500 nm LED lamp with adjustable illumination from 100 mW cm\(^{-2}\) to 1 mW cm\(^{-2}\), the light ideality factor is calculated according to

\[ n_L = \frac{q}{k_B T} \cdot \frac{dV}{d(\ln (L))} \]

where

- \( k_B \) represents Boltzmann constant
- \( T \) is the temperature
- \( L \) is the normalized light intensity

The electron collection efficiency (\( \eta_c \)) can be calculated from followed equations from IMVS and IMPS measurement:

\[ \tau_t = \frac{1}{2\pi f_{IMPS}} \]
\[ \tau_n = \frac{1}{2\pi f_{IMVS}} \]
\[ \eta_c = 1 - \frac{\tau_t}{\tau_n} \]

Where

- \( \tau_t \) is the effective electron transport time
- \( \tau_n \) is the electronic recombination lifetime,

\( f_{IMVS} \) and \( f_{IMPS} \) are the characteristic frequencies (that correspond to the peaks in the imaginary parts of the IMPS and IMVS Bode plots (see Figure S10))
Figure S1. X-ray diffraction patterns of ZnO seeds and hydrothermally grown ZnO NW arrays;

Figure S2. SEM images of (a) vertical ZnO NRs and (b) random ZnO NRs with low magnification which showed homogeneous and large-area uniformity.
Figure S3. SEM images of vertical ZnO NRs with different reaction time from 10 min to 60 min.

Morphology and crystal configuration of ZnO NW arrays:

The crystal qualities, morphology and crystalline orientation of our ZnO NWs are visualized by TEM images in Figure 1. The vertical ZnO NW arrays showed a distinct lattice structure confirming a lattice spacing of 0.52 nm along the growth directions, indicating a well-known (001) facet. The NCs-ZnO NW arrays display a lattice spacing of 0.26 nm, which is related to the (002) facet as shown in XRD patterns (Figure S1). This crystalline orientation is also consistent with SAED pattern (Figure 1c,d inset). The different distribution of NCs-ZnO seeds orientation give rise to the different growth direction of ZnO NW arrays, which provide us a controllable variable to monitor the influence of ZnO NWs orientation on CQDs/ZnO NWs
interfacial morphology and device performance.

**Figure S4.** SEM images of convective assembled CQD film on randomly oriented ZnO NRs after 4 layers CQDs deposition.

**Figure S5.** SEM images of CQD solid on ZnO NRs with different thickness and deposition technique. The surface morphology of CQDs ranged evidently at the first few layers. The spin-coated CQDs surface after 2 layers CQDs deposition show large cracks initially while the convective assembled CQDs show much better infiltrations.
Figure S6. (a) The schematic diagram of convective assembly setup and the SEM images of CQD film morphology optimized through (b) solvent selection, (c) solution concentration and (d) receding speed.
Figure S7. I-V curves of PbS CQD solar cells deposited by spin coating and convective assembly based on planar structured sol-gel ZnO layers. The spin-coated device demonstrates a PCE of 8.94%. The CA device presents a better $V_{oc}$ and $FF$ with an enhanced PCE of 9.35%.

Figure S8. (a) XRD spectra and (b) TEM image of PbS CQD; (c) The absorbance and photoluminescence spectra of CQDs in hexane solution; (d) the absorbance of CQD films prepared through different conditions measured under reflection mode.
Figure S9. (a) The illustration of OBHJ devices prepared through convective assembly and spin coating. The effective infiltration of CQDs into NW interspaces and the elimination of pinholes lead to larger effective thickness of CQD film. (b) External quantum efficiency (EQE) spectra of CQD devices prepared under different conditions. The integrated current density of each device is listed.
Figure S10. Bode plot of the imaginary current part of spin coating devices on vertical aligned ZnO NWs (a, b), convective deposited devices on random oriented NWs (c, d), and convective assembled devices on vertical NWs (e, f) using IMVS (a,c,e) / IMPS (b,d,f) measurement under various illumination intensities. The IMPS represents the frequency where each imaginary part reaches its minimum value.
Figure S11. The PL spectra of ZnO NW arrays with/without ABA treatment. After surface modification with ABA monolayer, the broad defects-induced emission was significantly suppressed. The effective carboxylate binding of aminobenzoic acid with zinc ion could possibly reduce the oxygen vacancies on ZnO NW surfaces and suppress the interfacial recombination in CQD OBHJ devices.

Figure S12. (a) Thermal stability of PbS CQD devices based on planar structure ZnO NCs under ambient air. The devices were continuously heated at 85 °C; (b) Comparison of histograms of PCEs for the CQD OBHJ solar cells prepared through different conditions.
Table S1. The fitting result of EIS parameters obtained from different devices.

| Device Type          | $R_s$ (Ω) | $R_tr$ (Ω) | $R_{ct}$ (Ω) | $C_{geo}$ (nF) | $C_μ$ (F) | $τ_{oc}$ (s) |
|----------------------|-----------|------------|--------------|----------------|-----------|-------------|
| Vertical NWs-Spin    | 22.34     | 84.5       | 13.59        | 2.72           | 0.15      | 2.03        |
| Random NWs-CA        | 19.52     | 74.8       | 12.38        | 47.1           | 0.18      | 2.22        |
| Vertical NWs-CA      | 26.64     | 60.06      | 10.87        | 48.3           | 1.29      | 14.0        |
| Vertical NWs ABA-CA  | 22.37     | 53.24      | 7.01         | 52.9           | 1.07      | 7.50        |

Table S2. The optimization of ABA modification with different conditions. The modification was conducted with water or methanol solvent under ambient air or N$_2$ filled glove box.

| Deposition method   | Solvent/Atmosphere | Dipping time | $V_{OC}$ (V) | $J_{SC}$ (mAc$m^{-2}$) | $FF$ | PCE  |
|---------------------|--------------------|--------------|--------------|------------------------|------|------|
| CA                  | Controlled         |              | 0.49         | 27.3                   | 61.3 | 8.26 |
| ③ABA-water-air      | 1min               | 0.35         | 15.3         | 42.5                   | 2.29 |
| ①ABA-methanol-air   | 1min               | 0.49         | 26.9         | 53.3                   | 7.09 |
| ②ABA-methanol-N$_2$ | 1min               | 0.53         | 27.3         | 62.7                   | 9.02 |
| ②ABA-methanol-N$_2$ | 30min              | 0.52         | 26.7         | 59.0                   | 8.15 |
| ②ABA-methanol-N$_2$ | 1h                  | 0.52         | 27.5         | 60.1                   | 8.55 |
| ②ABA-methanol-N$_2$ | 6h                  | 0.50         | 25.4         | 41.0                   | 5.23 |

(1) Le Berre, M.; Chen, Y.; Baigl, D., From Convective Assembly to Landau-Levich Deposition of Multilayered Phospholipid Films of Controlled Thickness. *Langmuir* **2009**, 25 (5), 2554-2557.