## **Supporting information**

# Chemical processing of three-dimensional graphene networks on transparent conducting electrodes for depleted-hetereojunction quantum dot solar cells

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#### 1. Materials and method

#### **1.1 Materials**

Lead(II) oxide powder (PbO, 99%), oleic acid (OA, technical grade 90%), dimethyl formamide (DMF), Hydrochloric acid (HCl) anhydrous toluene, octane, methanol, isopropyl alcohol, Triton X-100 were purchased from Merck, Germany. Bis(trimethylsilyl) sulfide (TMS, Strem, 97% purity), 1-octadecene (ODE, Sigma-Aldrich, technical grade 90%), zinc acetate dihydrate (Sigma-Aldrich), mercaptopropionic acid (MPA, Sigma-Aldrich), TiO<sub>2</sub> paste (Dyesol 18NRT, Dyesol), and titanium tetrachloride (Sigma-Aldrich) were used as received without further purification.

#### 1.2 Synthesis of graphene oxide

Modified Hummers method was used to synthesize graphene oxide (GO) using graphite powder.<sup>[1]</sup> First, 2.0 g graphite powder and 1 g NaNO<sub>3</sub> and 46 ml cooled H<sub>2</sub>SO<sub>4</sub> (0°C) were mixed. Then, 6 g KMnO<sub>4</sub> was added dropwise during stirring for 2 hours and then stirred in a water bath (30°C) for 30 minutes. Afterward, 100 ml deionized water was slowly added and the temperature was increased to 98°C. The mixture was maintained at this temperature for 30 minutes. Finally, the reaction was terminated by adding H<sub>2</sub>O<sub>2</sub> solution (20 ml, 30%) followed by adding 300 ml deionized water until the color of the mixture was changed to brilliant yellow, indicating the oxidation of pristine graphite to GO. Afterward, the mixture was filtered and washed with diluted HCl to remove metal ions. The product was washed several times with distilled water until the pH reached 7 and finally dried in Petri dishes at room temperature (Fig. S1).

#### 1.3 Synthesis of PbS quantum dots

In order to synthesize PbS QDs, a solution of  $210 \,\mu$ L of TMS in 10 mL of ODE was swiftly injected into a three-necked flask containing 0.45 g of PbO and 18 mL of ODE which were mixed at 110 °C for 16 h. The temperature and reaction time were 120 °C and 10 min, respectively. The reaction product was separated by centrifugation (4000 rpm), washed several times with methanol and acetone, and re-dispersed in octane.

For the Cd doping of PbS QDs, we adapted the procedure previously reported in literature for PbS QDs.<sup>[2]</sup> A solution of 2 mmol of CdCl<sub>2</sub>, 0.1 g TDPA and 10 ml oleylamine were mixed in a flask and maintained at 100°C for 30 min to obtain a transparent light-yellow solution. Then, 4 ml of Cd-containing solution were mixed by 12 ml of the octane solution of PbS QDs (80 mg/mL) and maintained at 60 °C for 2 h, followed by washing and re-dispersion of the resulted QDs in octane.

#### 1.4 Synthesis of ZnO/graphene QDs

0.92 g Zinc acetate dihydrate was dissolved in 200 ml of DMF. Then, a solution of 40 mg GO dissolved in DMF using ultrasonication was added dropwise during stirring to form a stable precursor. Afterward, this solution was maintained at 95 °C for 5 hours until the color of solution changed to white-greyish and as a result, ZnO/graphene QDs formed. The product was washed several times with ethanol by centrifugation, and finally with DI water. The final ZnO/graphene QDs was obtained after drying the product at 55 °C.

#### 1.5 Synthesis of 3DGN

In order to synthesize 3DGN, an acidic solution of HCl (5% wt) was used to dissolve the ZnO core from ZnO/graphene QDs. In this regard, ZnO/graphene QDs were dispersed and maintained in this acidic solution at room temperature for 2 h. Finally, the product was washed several times with DI water by centrifugation and redistributed in ethanol.

#### **1.6 Device fabrication**

FTO glasses with ohmic sheet resistance of 8  $\Omega$  were provided from HARTFORD GLASS, USA. They were cleaned by immersion in de-ionized (DI) water (Milipore, 18 M  $\Omega$ -cm) containing 3 vol% Triton X-100 and sonicated for 30 min, rinsed with water, sonicated in isopropanol for 30 min, sonicated in a DI batch for 30 min and finally dried under nitrogen flow.

A 300-nm-thick mesoporous TiO<sub>2</sub> layer composed of 20 nm-sized particles was spin-coated on FTO substrates at 5000 rpm for 45 s using a commercial  $TiO_2$  paste (Dyesol 18NRT, Dyesol) dispersed in ethanol. After drying at 125 °C, the TiO<sub>2</sub> films were annealed at 500 °C for 30 min and cooled to room temperature, followed by TiCl<sub>4</sub> treatment.<sup>[2]</sup> In this regard, the substrate immersed in 50 mM TiCl<sub>4</sub> aqueous solutions for 30 min at 70 °C, and rinsed with DI water and ethanol, followed by annealing at 550 °C for 30 min in air to form a n-type layer of TiO<sub>2</sub>. Then, a 70-nm-thick layer of 3DGN were coated on TiO<sub>2</sub> substrate using electrophoretic deposition (EPD). For the EPD process, the electrodes were mounted parallel to each other with a distance of 10 mm in a 25 ml of 3DGN solution. The applied voltage (DC) was 100 V and the duration of the process was 20 min. Afterward, the substrate was washed by DI water and dried using nitrogen gas. In order to fabricate PbS QDs on the substrate, deep coating method was employed. Thus, the substrates were first dipped into 30 mL beakers containing 15 mL solution of 0.05% MPA in methanol for 5 s, then left to dry for 5 min. Then, the substrates were dipped into a beaker containing 15 mL of 7.5 mg/mL Cd-doped PbS quantum dots in hexane for 30 s, and left to dry for 5 min. Afterward, the substrates were dipped into a beaker containing 25 mL of 0.2% MPA in methanol solution (solid-state exchange) for 3 s followed by 60 s drying. Finally, the substrates were rinsed in a beaker containing 25 mL of pure methanol for 5 s and dried for 2 min. These processes were repeated for 12 times. Finally, the top contact MoO<sub>3</sub>/Au layers (25 nm/100 nm) were deposited by thermal evaporation at a rate of ~0.8  $\overset{\circ}{A}$ /s.

Cd-doped PbS QDs layer was deposited on TiO<sub>2</sub> substrate was as a reference sample and its process was reported in the literature.<sup>[2]</sup>

#### **1.7 Materials characterization**

In order to study the structure and phase characterization, High-resolution transmission electron microscope (HRTEM, JOL, JEM-2100, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD, Stone Sandi P, USA) utilizing a Cu  $K\alpha$  radiation were used, respectively. Infrared spectra were recorded on a Perkin-Elmer Fourier transformed infrared spectroscope (FTIR, Spectrum RX, USA). A InVia (Renishaw AB, Sweden) spectrometer with 514.5 nm wavelength incident laser light was employed to measure Raman spectra. X-ray photoelectron spectroscopy (XPS) were measured on a hemispherical analyzer with an Al Ka Xray source (1486.6 eV) operated at 10<sup>-7</sup> Pa. Optical measurements (absorption and Photoluminescence (PL) spectra) were recorded on a Varian Carry 500 spectrometer (Varian, USA) and an FLS920P fluorescence spectrometer (Edinburgh Instruments) equipped with a cryogenically cooled photomultiplier (R5509-43, Hamamatsu), with a 450 W continuous xenon arc lamp as the excitation source for steady-state spectra and a picosecond pulsed diode laser (EPL-405, excitation wavelength 405 nm, pulse width: 49 ps) for lifetime measurements. PL decay curves were fitted using the stretched exponential function  $I(t) = I_0 e^{-(t/\tau)^{\beta}}$ , where  $\beta$  is a stretch parameter and  $\tau$  is the decay time. Field-emission scanning electron microscopy (FESEM, Hitachi S4160, Japan) and atomic force microscopy (AFM, JPK Co, Germany) were used to study the thickness, morphology and roughness of the films. The work function and valence band of semiconducting ZnO/G layer were obtained from ultraviolet photoelectron spectroscopy (UPS, AXIS NOVA, Kratos Analytical Ltd, UK) by employing He I (21.2 eV) as the photon source. Electrochemical Impedance Measurements (EIS) were performed by an Autolab PGSTAT30 (EcoChemie B.V., Utrecht, Netherlands) with a frequency range from 1 MHz down to 0.1 Hz at bias potentials 0.6 V (with a 10 mV sinusoidal AC perturbation). All measurements were done at room temperature.

In order to further study the role of 3DGN layer, we employed electrochemical impedance spectra (ESI) analysis, as shown in Fig. S8. As can be seen, Nyquist curves have been plotted for the devices with and without 3DGN layer (Z' vs. -Z''), where Z' and Z'' are the real and imaginary parts of the cell impedance, respectively. The radius of the semicircles of the device with 3DGN layer is smaller than device based on TiO<sub>2</sub> electrode, suggesting that 3DGN layer reduces the charge-transfer resistance. The values of the Ohmic resistance and charge-transfer resistance are 13.6 and 298.3 Ohm in device with 3DGN, respectively, which are lower than those of the corresponding conventional device 17.7 and 387.9 Ohm, respectively.

#### 1.8 Photovoltaic performance of solar cells

The solar spectrum at AM1.5G was simulated with a Xe lamp and filters with an intensity of 100 mWcm<sup>-2</sup>. A Keithley 2400 (USA) instrument was used to measure the current-voltage (J-V) data. The voltage range was between -1 and +1 V with a step size of 0.02 V and a delay time of 150 ms at each point. The accuracy of the power measurement was expected to be  $\pm$ 5%. External quantum efficiency (EQE) spectra were obtained versus wavelength under a constant white light bias of approximately 5mWcm<sup>-2</sup> using an array of white light-emitting diodes. The excitation beam coming from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double

monochromator (Jobin Yvon Ltd) and chopped at approximately 2 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier.

### References

[1] J. Hummers, S. William and R. E. Offeman. JACS, 1958, 80, 1339.

[2] A. H. Ip, S. M.Thon, S. Hoogland, O. Voznyy, D. Zhitomirsky, R. Debnath, E. H. Sargent. *Nat. Nanotech.* 2012, 7(9), 577.

 Table S1 Fitting parameters of the corresponding PL decay curves.

Electrode	τ (ns)	$\boldsymbol{\beta}_1$	<b>B</b> <sub>2</sub>	B <sub>3</sub>	X
Conventional device	15.2	17641.7	7234.7	3462.1	1.07
Device based on 3DGN	3.1	13256.5	4103.5	785.9	1.12





Fig. S1: (a) AFM image of graphene oxide sheets, (b) Raman spectra of graphitic materials.



Fig. S2: The EDS of hybrid ZnO/graphene QDs shows the quality and composition of the dots.

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Fig. S3: The schematic fabrication process of 3DGN from ZnO/graphene QD.



**Fig. S4:** HRTEM images, (a) low magnification, (b) lattice scale fringes, (c) selected area electron diffraction pattern (SAD), and (d) XRD pattern of PbS QDs.



Fig. S5: The EDS of PbS QDs shows the quality and composition of the dots.



**Fig. S6:** Optical properties of the PbS QDs. (a) The absorption spectrum of Cd-doped PbS QDs, (b) PL spectra of Cd-doped PbS QDs.



Fig. S7: Steady photoluminescence spectra of device based on 3DGN layer (red curve) and conventional device (black curve).



**Fig. S8:** Electrochemical impedance spectra of device based on 3DGN layer (red curve) and conventional device (black curve).