PbS Colloidal quantum dots as the effective hole transporter for planar heterojunction perovskite solar cells

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Synthesis of CH_3NH_3I: Methylamine (33 wt % in methanol; Alfa) and hydroiodic acid (57 wt % in water; Alfa) were stirred at 0 °C for 2 h and then the solvent was evaporated using a rotary evaporator after the reaction. A white powder, methylammonium iodide, was obtained and recrystallized with ethanol and precipitated with diethyl ether. This process was repeated three times, and finally the products were dried at 60 °C in a vacuum for 24 h.

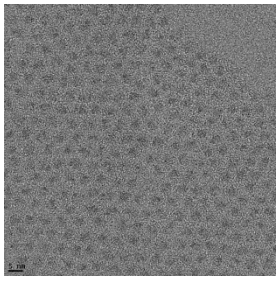
Synthesis of PbS CQDs：0.45 g PbO (Alfa), 1.45 g Oleic acid (OA) (Alfa), 15 g octadecene (ODE) (Alfa) were added into 50 ml three-neck flask, and pumping at 90 °C for 12 h to prepare Pb precursor. 180 ul bis(trimethylsilyl) sulfide (TMS) (Sigma) was added into 10 ml ODE which was pumped in advance to remove H_2O and O_2. We synthesized four batch PbS CQDs by injected TMS into Pb precursor by adjusting the injection temperatures and reaction time.

Table 1.

peak	PbO	TMS	ODE	OA	Injected T	Reaction time
890 nm	0.45 g	180 ul	15 g	1.45 g	70 °C	120 s
1050 nm	0.45 g	180 ul	15 g	1.45 g	120 °C	120 s
1150 nm	0.45 g	180 ul	15 g	1.45 g	140 °C	60 s
1500 nm	0.45 g	180 ul	15 g	1.45 g	180 °C	30 s

Preparation of p-type PbS film: 8 mg/ml PbS CQDs in hexane was spin-coated on patterned ITO glass for 20 s at 2500 rpm, and then the substrate was dipped into 10 mg/ml trimethylammonium hydroxide (TMAOH) methanol solution for 10 s to remove OA ligand capped on PbS CQDs. Then the film was rinsed with methanol. This process was repeated three times. As-prepared PbS CQDs film was annealed on 70 °C hotplate in air for 12 h.

Fig.1 TEM image of the 1-PbS CQDs



Devices fabrication: All device fabrication processes were carried out inside a nitrogen- filled glovebox with oxygen and moisture levels of <0.5 ppm. 300 mg/mL PbI_2 solution was prepared by

dissolved PbI_2 in anhydrous N,N-dimethylformamide (DMF; Alfa) at 60 °C and stirred for 12 h. Then PbI_2 solution was spin-coated on PbS CQDs film for 30 s at 3000 rpm, and heated on 70 °C hotplate for 30 min to remove DMF. When the film cooled to room temperature, the PbI_2 film was dipped into 10 mg/ml CH_3NH_3I isopropanol (IPA) solution for 45 s at 50 °C, then rinsed with anhydrous IPA for 10 s. 20 mg/ml PCBM([6,6]-phenyl-C61-butyric acid methyl ester) in chloroform was spin-coated onto $CH_3NH_3PbI_3$ film for 30 s at 3000 rpm. The top 100 nm Al electrode was prepared by thermal evaporated.

Measurement and Characterization. UV-VIS-NIR spectra were recorded on a Perkin Elmer model Lambda 750. Measurement of the current density −voltage characteristics of the devices was carried out using a Keithley 2400 (I− V) digital source meter under a simulated A M 1.5 G solar irradiation at 100 mW/cm^2 (Newport, AAA solar simulator, 94 023A-U) inside the glovebox. Device area is 7.25 mm^2. Tapping mode atomic force microscopy (AFM) was performed using a Veeco multimode V instrument. Scanning electron microscopy (SEM) images were obtained using a FEI Nova NanoSEM 450. X-ray diffraction (XRD) results were acquired using a Phillips X' Pert PRO. Photoluminescence spectra were obtained by using an automated spectrofluorometer (FluoMax, Horiba Jobin-Yvon). The external quantum efficiency was measured using power source(300W xenon lamp of Newport, Oriel 69911) with a Monochromator(Oriel, model 74004).

Table 2

Control device performance: using different size of PbS CQDs but all without perovskite absorbers

sample	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	PCE(%)
1-PbS	0.37	2.24	0.38	0.31
2-PbS	0.34	2.78	0.39	0.35
3-PbS	0.33	2.83	0.37	0.34
4-PbS	0.27	2.54	0.35	0.24