

Methods are described in roughly the order they appear in the results

Standard methods are cited

Methods

Synthesis of colloidal PbS QDs. The synthesis of oleic-acid-capped PbS QD with a first absorption peak at $\lambda = 901$ nm was adapted from the literature^{11,29}. Lead acetate (11.38 g) was dissolved in 21 ml of oleic acid and 300 ml of 1-octadecene at 100 °C. The solution was degassed overnight and then heated to 150 °C under nitrogen. The sulphur precursor was prepared separately by mixing 3.15 ml of hexamethyldisilathiane and 150 ml of 1-octadecene. The reaction was initiated by rapid injection of the sulphur precursor into the lead precursor solution. After synthesis, the solution was transferred into a nitrogen-filled glovebox. QDs were purified by adding a mixture of methanol and butanol, followed by centrifugation. The extracted QDs were re-dispersed in hexane and stored in the glovebox. For device fabrication, PbS QDs were further precipitated twice with a mixture of butanol/ethanol and acetone, respectively, and then re-dispersed in octane (50 mg ml⁻¹).

Synthesis of ZnO nanoparticles. ZnO nanoparticles were synthesized according to the literature³⁰. Zinc acetate dihydrate (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. The potassium hydroxide solution was slowly added to the zinc acetate solution and the solution was kept stirring at 60 °C for 2.5 h. ZnO nanocrystals were extracted by centrifugation and then washed twice by methanol followed by centrifugation. Finally, 10 ml of chloroform was added to the precipitates and the solution was filtered with a 0.45 µm filter.

Device fabrication. Patterned ITO substrates (Thin Film Device Inc.) were cleaned with solvents and then treated with oxygen plasma. ZnO layers (120 nm) were fabricated by spin-coating a solution of ZnO nanoparticles onto ITO substrates. PbS QD layers were fabricated by layer-by-layer spin-coating. For each layer, 10 µl of PbS solution was spin-cast onto the substrate at 2,500 rpm for

a xenon lamp (Thermo Oriel 66921) through a monochromator into the optical fibre and the photocurrent was recorded using a lock-in amplifier (Stanford Research System SR830). Both current–voltage and EQE measurements were performed under an inert atmosphere unless stated otherwise. Devices were stored in ambient air between each measurement.

Ultraviolet photoelectron spectroscopy. PbS-TBAI and PbS-EDT samples for UPS measurements were fabricated in air using six layer-by-layer spin-coating steps to obtain 110 nm-thick PbS films on glass/Cr(10 nm)/Au(80 nm) substrates. For PbS-EDT-thickness-dependent UPS, a diluted PbS solution (10 mg ml^{-1}) was used to obtain the thinner PbS-EDT layers on PbS-TBAI films. The samples were then stored in air overnight before UPS measurements. UPS measurements were performed in an ultrahigh vacuum chamber (10^{-10} mbar) with a He(I) (21.2 eV) discharge lamp and have a resolution of 0.1 eV. Carbon tape was used to make electrical contact between the Cr/Au anode and the sample plate. A -5.0 V bias was applied to the sample to enable accurate determination of the low-kinetic-energy photoelectron cut-off. Photoelectrons were collected at 0° from substrate normal and the spectra were recorded using an electron spectrometer (Omicron). The conduction band edge energies were calculated by adding the optical bandgap energy of 1.33 eV determined from the first exciton absorption peak in the QD thin films to the valence band edge energies. The $E_F - E_V$ values have an error bar of $\pm 0.02 \text{ eV}$ resulting from curve fitting.

Details necessary for replication

15 s. A TBAI solution (10 mg ml^{-1} in methanol) was then applied to the substrate for 30 s, followed by three rinse-spin steps with methanol. For PbS-EDT layers, an EDT solution (0.02 vol% in acetonitrile) and acetonitrile were used. All the spin-coating steps were performed under ambient condition and room light at room temperature. The thicknesses of each PbS-TBAI and PbS-EDT layer are about 18 nm and 23 nm, respectively, as determined by a profilometer (Veeco Dektak 6M). The films were stored in air overnight and then transferred to a nitrogen-filled glovebox for electrode evaporation. MoO_3 (Alfa; 25 nm thick), Al or Au electrodes (100 nm thick) were thermally evaporated onto the films through shadow masks at a base pressure of 10^{-6} mbar. The nominal device areas are defined by the overlap of the anode and cathode to be 1.24 mm^2 . Larger-area devices (5.44 mm^2) have also been fabricated and show similar performance (Supplementary Figs 12 and 13). For certification of the larger area device, a 3 mm^2 mask was attached to the device to define the device area.

Device characterization. Current–voltage characteristics were recorded using a Keithley 2636A sourcemeter under simulated solar light illumination (1-Sun, 100 mW cm^{-2}) generated by a Newport 96000 solar simulator equipped with an AM1.5G filter. The light intensity was calibrated with a Newport 91150 V reference cell before each measurement. The error in efficiency measurements is estimated to be below 7%. EQE measurements were conducted under chopped monochromatic light from an optical fibre in an underfilled geometry without bias illumination. The light source was provided by coupling the white light from