CdZnSe@ZnSe colloid alloy quantum dots for high-efficiency all-inorganic perovskite solar cells

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Experimental section

Synthesis of CdZnSe cores

0.5 mmol of CdO, 5.0 mmol ZnAc, 3.0 mL oleic acid (OA) and 8.0 mL of octadecene (ODE) were loaded in a 100 mL round-bottom flask. After vacuum pumping for 30 min, the mixture was heated to 100 °C under nitrogen. The mixture was heated to 300 °C under nitrogen to obtain a clear mixed solution. Subsequently, 3.0 mL Se stock solution (Se stock solution was prepared by dissolving 0.8 mol Se powder in 5 mL 1-ODE) was injected quickly into the flask.

Synthesis of CdZnSe@ZnSe QDs

When the synthesis of CdZnSe core was completed, the solution was heated to 310 °C, then various amount (1.0 mL, 2 mL and 2.5 mL) Se stock solution (Se stock solution was prepared by dissolving 1.2 mol Se in 5 mL ODE) as Se precursor was injected slowly into the flask. After centrifugation from the reaction solution, followed by drying under 40~50 °C for 2 h in a vacuum chamber,

CdZnSe@ZnSe QD powder can be obtained.

Synthesis of the TiO₂ paste.

The TiO₂ nanoparticles used in this work were prepared by a hydrothermal processing, as described elsewhere.^[S1] In details, 10 mL of titanium tetrabutanolate was dropwise addition into 100 mL of deionized water under vigorous agitation at room temperature for 30 min to obtain dehydrated filter powders. Subsequently, 10 mL of acetic acid and 0.8 mL of nitric acid were added dropwise to these filter powders. After agitating for 15 min at 80 °C, 160 mL of deionized water was added. When the reactant solution became semi-transparency, the obtained solution was undergone hydrothermal treatment at 200 °C for 12 h. Then, 0.4 g of commercial P25 was added and sonicated for 30 min and then heated at 200 °C for another 12 h. The resultant colloid was finally mixed with 0.8 g of poly(ethylene glycol) ($M_w = 20,000$) and 1 mL of OP emulsifier and then concentrated to 40 mL at 80 °C.

Solar cell fabrication.

All the processes were conducted in air atmosphere without humidity control. Prior to fabrication of solar cells, an FTO coated glass was etched with zinc powder and HCl (2 M) to obtain the desired pattern and then thoroughly rinsed in detergent, acetone, isopropanol, ethanol and deionized water. A compact TiO₂ (*c*-TiO₂) layer was deposited onto an FTO glass by spin-coating an ethanol solution of titanium isopropoxide (0.5 M) and diethanol amine (0.5 M) at 7000 rpm for 30 s and annealed in air at 500 °C for 2 h. The mesoporous-TiO₂ (*m*-TiO₂) layer was subsequently spin-coated on the *c*-TiO₂ surface using the as-prepared TiO₂ paste at 2000 rpm for 30 s and annealed in air at 450 °C for 30 min. Afterwards, the *c*-TiO₂/*m*-TiO₂ substrate was immersed in an aqueous solution of 0.04 M TiCl₄ at 70 °C for 30 min, and then annealed in air for another 30 min at 450 °C.

The perovskite film was fabricated by a multi-step solution-processed technology. A N,N-

dimethylformamide (DMF) solution of 1 M PbBr₂ containing various lanthanide ions with stoichiometric ratio ranging from 1% to 5% was spin-coated onto the *m*-TiO₂ substrate at 2000 rpm for 30 s under 90 °C. After being dried at 90 °C for 1 h, 0.07 M CsBr methanol solution was spin-coated onto PbBr₂ film at 2000 rpm for 30 s and continuingly heated at 250 °C for 5 min. This process was repeated for several times to obtain the ideal perovskite films. The obtained perovskite films were rinsed with isopropanol and dried at 250 °C again for 5 min. Then, the CdZnSe@ZnSe QDs were spin-coated onto the CsPbBr₃ film at 2000 rpm for 30 s, followed by drying at 85 °C for 5 min to evaporate cyclohexane. Finally, a carbon back-electrode was deposited on the perovskite film with an active area of 0.09 cm⁻² by a doctor-blade coating method. The fabrication processes for pristine device was similar except for the spin-coating of 1 M PbBr₂ DMF solution onto *m*-TiO₂ substrate at 2000 rpm for 30 s.

Characterizations.

Transmission electron microscope (TEM) images were acquired on a Tecnai G2 F20 microscope. The morphology and element ratio of the perovskite films were obtained using a field-emission scanning electron microscope (SEM, S4800, Hitachi). The X-ray diffraction (XRD) patterns of the as-prepared films were recorded using a X-ray diffractometer (Bruker D8 ADVANCE) with Cu K α ($\lambda = 1.5406$ Å) radiation. Ultraviolet-visible (UV-vis) absorption spectra of various perovskite films were characterized employing a Meipuda UV-3200 spectrophotometer. The time-resolved PL decay characterizations were conducted with a Horiba spectrometer excited by 370 nm laser. The IPCE spectra of various devices were recorded by IPCE kit developed by Zolix Instruments Co., Ltd. The *J-V* curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) under AM 1.5G simulated solar illumination (100 mW cm⁻², calibrated by a standard silicon solar cell). A black mask was applied on the surface of cell device to avoid stray light.

References

1 Y. Duan, Q. Tang, Z. Chen, B. He and H. Chen, *J. Mater. Chem. A*, 2014, **2**, 12459-12465.



Fig. S1 Normalized time-resolved PL decay curves of CdZnSe@ZnSe QDs.



Fig. S2 The date statistics of efficiencies from various devices.



Fig. S3 *J-V* plots of 2.16 eV-QDs tailored all-inorganic PSC measured in the forward and reverse scanning modes.



Fig. S4 (a), (c), and (e) The corresponding $(Ahv)^2$ vs energy (hv) curves of various QDs. (b), (d), and (f) Cyclic voltammetry curves of CuInSe@ZnSe QDs to characterize the HOMO values.