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Supporting Information

Reversible Modulation of CsPbBr₃ Perovskite Nanocrystal/Gold

Nanoparticle Heterostructures

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Experimental Section

The preparation of CsPbBr₃ NCs was referring to Kovalenko's group with few modifications.¹

1. Preparation of precursors:

0.0407 g cesium carbonate (CsCO₃, Aladdin, 99.9%) was dissolved in 2 mL 1-octadecene (ODE, Aladdin, 90%) with 125 μL oleic acid (OA, Aladdin, 85%). The mixture was dried for 1 h at 120 °C, then was heated up to 150 °C under nitrogen atmosphere to form a clear solution.

2. Synthesis of CsPbBr₃ NCs:

0.069 g lead bromide (PbBr₂, HWRK ChemCo., LTO, 99.0%), 0.5 mL oleic acid and 0.5 mL oleylamine (Aladdin, 80-90%) were mixed with 5 mL 1-octadecene in a three-neck flask. Then, the flask was attached to a Schlenk line, and at least three evacuate-refill cycles were conducted to generate a nitrogen atmosphere at 120 °C for one hour. The reaction solution was further heated up to 170 °C in order to completely dissolve PbBr₂. Then 0.4 mL of precursors (keep the temperature above 100 °C before injection) were quickly injected into the as-prepared reaction solution. After ten seconds, the reaction solution was cooled immediately with an ice-water bath to room temperature. The resulting solution was mixed with 4 times of ethyl acetate (Tianjin Concord Chemical Reagent Co., Ltd., HPLC) for further purity. After centrifugation (10 min, 9500 rpm), the supernatant of the resulting mixture was discarded, and the NCs precipitates at the bottom were re-dispersed in toluene (Tianjin Liuchang Chemical

Reagent Co., Ltd., spectroscopic grade) to form a bright green colloidal solution. No additional washing step was performed in following experimental process.

3. The modulation of CsPbBr₃ NCs:

2 mg of gold (III) bromide (Aladdin, 99%) was dispersed in 3 mL of toluene to form the gold precursor solution. 1-dodecanethiol (Adamas, 98%) was diluted in toluene before use. 250 µM of fresh prepared gold precursor was mixed with CsPbBr₃ NCs (0.3 µM) in toluene, and the resulting solution was incubated at room temperature for 5 min to form CsPbBr₃/Au NP heterostructures. Fluorescence spectra were recorded to monitor the formation of CsPbBr₃ NC/Au heterostructures. Upon the addition gold precursor solution, the colour of CsPbBr₃ NCs turned to dark brown immediately. When 1.0 mM 1-dodecanethiol was subsequently added to the CsPbBr₃ NC/Au heterostructures solution, CsPbBr₃ NCs regenerate with the appearance of bright green solution colour in minutes. The above modulation procedures were repeated for cycles. During the cycles, the total volume is kept constant at 600 µL with toluene to compensate the generated concentration differences of CsPbBr₃ NCs. All experimental operations were performed under ambient conditions.

4. Characterization Methods:

UV-Vis absorption spectra were recorded using a UV-3900 spectrophotometer (HITACHI, Japan). PL spectra were recorded with an F-4600 fluorescence spectrophotometer (HITACHI, Japan). The value of the curve corresponded to same concentration of initial CsPbBr₃ NCs was normalized as 1. Lifetime experiments were carried out with a FLS 920P steady state and transient state fluorescence spectrometer using a time correlated single photon counting (TCSPC) system equipped with a femtosecond laser. Powder X-ray diffraction patterns (PXRD) were measured with D/max-2500 powder diffractometer (Rigaku) using Cu K α radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) images were recorded using Talos F200X transmission electron microscope operated at 200 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) spectra were taken with an Axis Ultra DLD spectrometer.



Fig.S1 UV-vis absorption (A) and PL emission (B) spectra of $CsPbBr_3 NCs$ upon the addition of 1-dodecanethiol with the concentration of 0, 1 mM, 7 mM, respectively.



Fig.S2 PL spectra (A) and corresponding histogram (B) of the system depicted the 4 cycles successive modulations of CsPbBr₃ NC/Au NP heterostructures by sequentially adding of AuBr₃ (b, d, f, h) and 1-dodecanethiol (c, e, g, i), respectively.



Fig.S3 UV-vis absorption spectra of as-prepared CsPbBr₃ NCs (a), the formed (b) and disengaged (c) CsPbBr₃ NC/Au heterostructures upon the addition of AuBr₃ and further addition of 1-dodecanethiol, respectively.



Fig.S4 Size distribution histogram of Au nanoparticle deposited on CsPbBr₃ NCs by counting 100 particles.



Fig.S5 TEM images of $CsPbBr_3 NCs$ after the addition of 7 mM 1-dodecanethiol.



Fig.S6 TEM size distribution analysis of as-prepared CsPbBr₃ NCs (A), formed (B) and disengaged (C) CsPbBr₃ NC/Au heterostructures upon the addition of AuBr₃ and further addition of 1-dodecanethiol, and CsPbBr₃ NCs after the addition of 1-dodecanethiol (D), respectively.

 Table S1: Time correlated single photon counting analysis of as-prepared CsPbBr₃ NCs, formed and disengaged

 CsPbBr₃ NC/Au heterostructures, respectively.

-	T ₁ (ns)	T₂(ns)	α1	α2	T _{average} (ns)
CsPbBr ₃	3.94	7.24	33.18%	57.91%	6.46
CsPbBr₃/Au NP heterostructures	1.03	2.56	50.55%	26.54%	1.90
the disengaged of heterostructures	3.35	6.62	40.31%	59.69%	5.79

 T_1 , and T_2 are the Life time of first and second components; $\alpha 1$ and $\alpha 2$ are the percentage of first and second components.; Taverages is the average lifetime calculated using the following equation.

$$T_{\text{average}} = (\alpha_1 T_1^2 + \alpha_2 T_2^2) / (\alpha_1 T_1 + \alpha_2 T_2)$$

References

L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, 15, 3692-3696.