

*Supporting information for*

## Synthesis and Optical Properties of CsCu<sub>2</sub>Br<sub>3</sub>-Cu<sup>0</sup> Nanoheterojunctions

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Keywords: CsCu<sub>2</sub>Br<sub>3</sub>-Cu<sup>0</sup>, heterojunction, localized surface plasmon resonance, lattice distortion, narrow-band dual emission

## Experimental section

### Materials

Cs<sub>2</sub>CO<sub>3</sub> (99.9% Aldrich), octadecene (ODE, 90%, Aldrich), oleic acid (OA, 90%, Aldrich), oleylamine (OM, 70%, Aldrich), PbBr<sub>2</sub> (99.999%, Aldrich), CuBr<sub>2</sub> (98.5%, Aldrich), cyclohexane (99.7%, Aldrich), anhydrous ethanol (99.7%, Aldrich).

All chemicals were used as received without further purification.

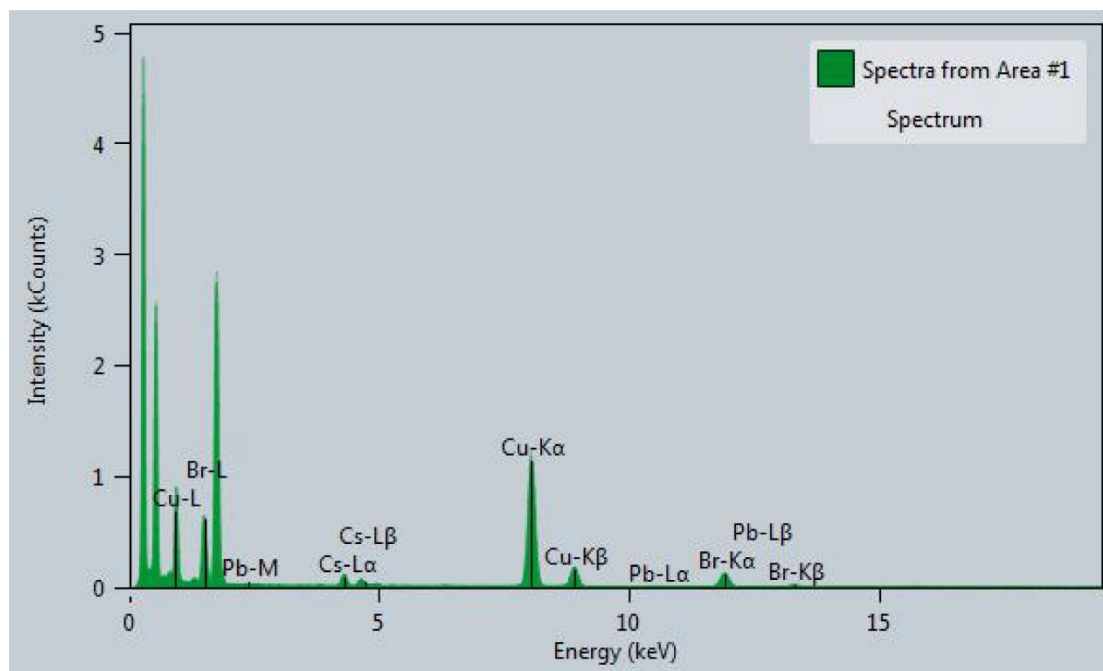
**Preparation of Cs-oleate solution:** 0.2035 g (0.62 mmol) Cs<sub>2</sub>CO<sub>3</sub> was loaded into a 50 mL three-necked bottle, along with 10 mL ODE, 1.5 mL OA were put into a pre-cleaned and dried under the protection of N<sub>2</sub>, and then heated at 120 °C until all Cs<sub>2</sub>CO<sub>3</sub> were dissolved.

**Preparation of CsCu<sub>2</sub>Br<sub>3</sub>-Cu<sup>0</sup> heterojunction NRs:** 0.0587 g (0.16 mmol) PbBr<sub>2</sub>, 0.1787 g (0.49 mmol) CuBr<sub>2</sub>, 5 mL ODE, 0.7 mL OA, 0.7 mL OM were put into a pre-cleaned and dried three-necked bottle, heated at 120 °C under vacuum and stirred for 15 minutes, and then heated to 200 °C under N<sub>2</sub> protection, kept stirring until the color of the solution in the three-necked flask turned dark brown. After continued stirring for 5 minutes, 1 mL Cs-OA solution was injected, and cooled to room temperature in an ice-water about 5 s. The reaction solution is first washed by ODE centrifugation, the upper solution is poured out, the lower precipitation is purified by cyclohexane centrifugation, and the upper solution is stored in a glass bottle.

**Preparation of CsCu<sub>2</sub>Br<sub>3</sub> NCs:** In the experiment of preparing CsCu<sub>2</sub>Br<sub>3</sub>, without adding PbBr<sub>2</sub>, and other conditions remain unchanged, CsCu<sub>2</sub>Br<sub>3</sub> nanocrystals are obtained.

## Characterization

Transmission electron microscopy (TEM) and high-resolution TEM investigations were carried out on a JEM 2100F. The X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima X-ray IV diffractometer using a Cu K $\alpha$  source at 3 deg·min<sup>-1</sup>. Time-resolved photoluminescence (PL) measurements were performed using a time-correlated single photon counting setup (TCSPC) utilizing SPC-130-EM counting module and BDL-488-SMN pico-second laser. Horiba Jobin Yvon iHR 320 spectrometer equipped with a Synapse CCD was used to acquire luminescence spectra. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS Ultra. Auger electron spectroscopy (AES) measurements were performed using a ESCALAB 250XI-AES.



**Figure S1.** EDX spectrum of the CsCu<sub>2</sub>Br-Cu<sup>0</sup> heterojunction NRs.

**Table S1.** Results of semi-quantitative analysis of composite elements of CsCu<sub>2</sub>Br<sub>3</sub>-Cu<sup>0</sup> heterojunction NRs.

Z	Element	Family	Atomic Fraction	Atomic Error	Mass Fraction	Mass Error	Fit Error
29	Cu	K	81.29%	9.10%	74.68%	6.14%	0.10%
35	Br	K	14.15%	2.24%	16.35%	2.28%	0.26%
55	Cs	L	4.34%	0.62%	8.33%	1.01%	0.29%
82	Pb	L	0.21%	0.03%	0.64%	0.08%	4.42%

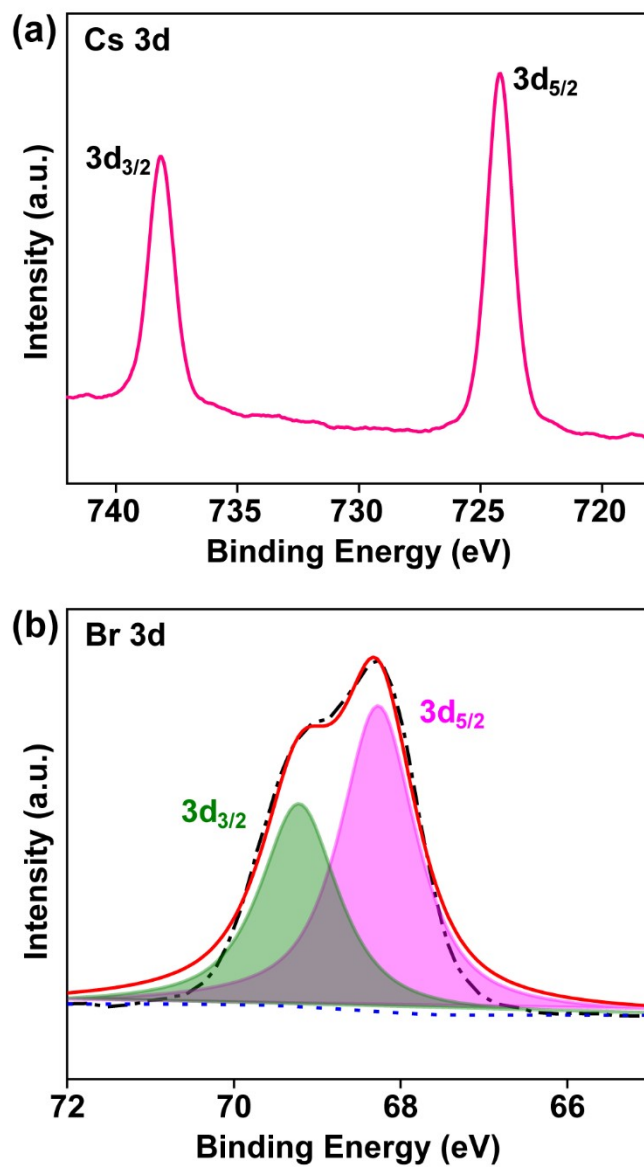
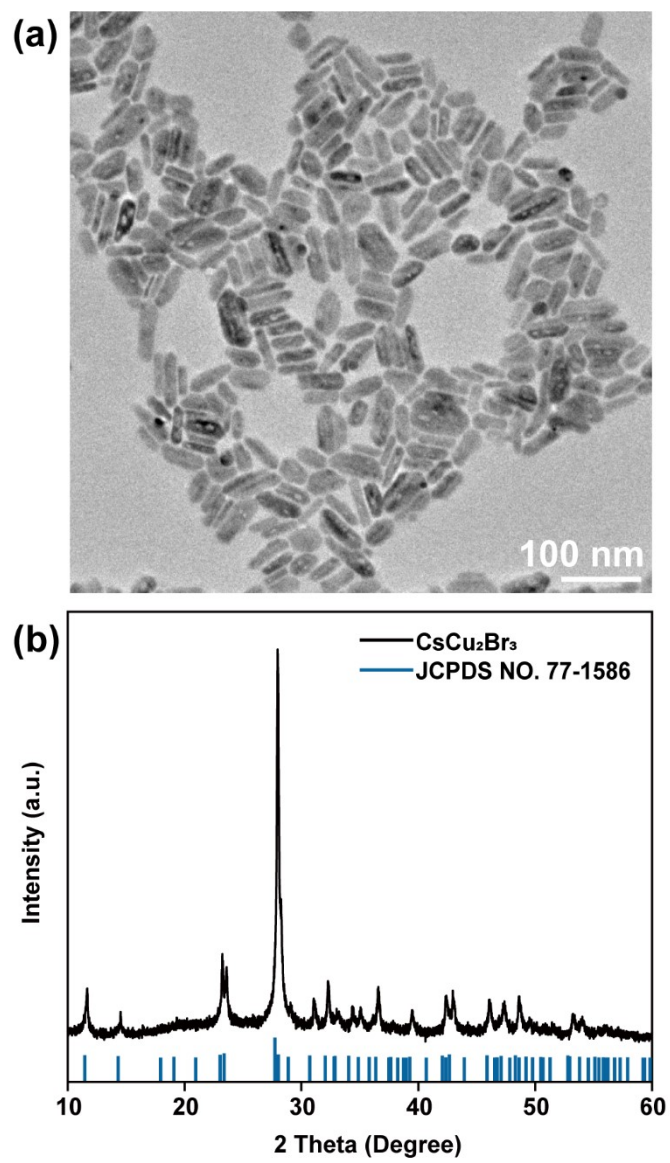


Figure S2. XPS spectra (a) Cs, (b) Br elements of  $\text{CsCu}_2\text{Br}_3\text{-Cu}^0$  heterojunction NRs



**Figure S3.** (a) TEM image of CsCu<sub>2</sub>Br<sub>3</sub>. (b) XRD pattern of CsCu<sub>2</sub>Br<sub>3</sub>.

**Table S2.** PL decay parameters of CsCu<sub>2</sub>Br<sub>3</sub>-Cu<sup>0</sup> heterojunction NRs and CsCu<sub>2</sub>Br<sub>3</sub> NCs.

<b>Sample</b>	<b>Wavelength</b>	<b><math>\tau_1</math> (ns)</b>	<b>A<sub>1</sub></b>	<b><math>\tau_2</math> (ns)</b>	<b>A<sub>2</sub></b>	<b><math>\tau</math> (ns)</b>
	<b>h (nm)</b>					
CsCu <sub>2</sub> Br <sub>3</sub> -Cu <sup>0</sup>	436	0.7588	1945.6686	3.7844	288.0584	2.0
CsCu <sub>2</sub> Br <sub>3</sub> -Cu <sup>0</sup>	460	1.1947	1754.5323	4.9225	350.1296	2.9
CsCu <sub>2</sub> Br <sub>3</sub>	500	2.2684	71112.155	15.3043	429.1701	2.8



**Table S3.** Lattice parameters of CsCu<sub>2</sub>Br<sub>3</sub> in the CsCu<sub>2</sub>Br<sub>3</sub>-Cu<sup>0</sup> heterojunction NRs

Space Group: Cmc <sub>2</sub> m (#63-1)			
a	9.8585 Å	$\alpha$	90.0000°
b	12.3479 Å	$\beta$	90.0000°
c	5.7771 Å	$\gamma$	90.0000°
Cu-Cu(a)	3.121 Å	Cu-Br1	2.390 Å
Cu-Cu(c)	2.888 Å	Cu-Br2	2.611 Å
V	703.256 Å <sup>3</sup>		