Electronic Supplementary Material (ESI) for Nanoscale.

Support Information

Ultra-long Distance Carrier Transportation in Bandgap-Graded CdS_xSe_{1-x} Nanowire Waveguides

Peng Fan,[a] Huawei Liu,[a] Xiujuan Zhuang,*[a] Weihao Zheng,[a] Cuihuan Ge,[a] Wei Huang,[a] Xin Yang,[b] Yong Liu,[a] Ying Jiang,[a] Xiaoli Zhu,[a] Anlian Pan*[b]

[a] Key Laboratory for Micro-Nano Physics and Technology of Hunan Province, Key Laboratory for Micro/Nano Optoelectronic Devices of Ministry of Education & Hunan Provincial Key Laboratory of Low-Dimensional Structural Physics and Devices, School of Physics and Electronic, Hunan University, Changsha 410082, People's Republic of China.

[b] Key Laboratory for Micro-Nano Physics and Technology of Hunan Province, State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Materials Science and Engineering, Hunan University, Changsha 410082, People's Republic of China

1. Experimental setup

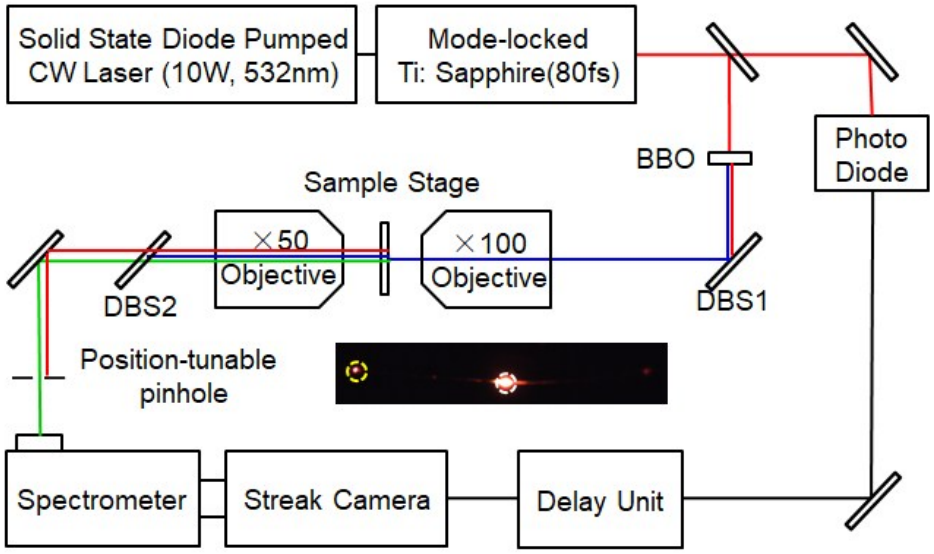

Fig. S1 Schematic diagram of the experimental setup. The PL signals originate from where other than selected area can be filtered by a position-tunable pinhole behind the microscope. Thus we can detect the PL signals only from waveguide. Inset：The real color PL image of the sample excited by a focoused laser with a spot with ~2 μm.

The system used to detect the the spatial and time resolved photoluminensence is a streak camera combined with a confocal microscope. A beam of the femto laser is focus to the sample through the confocal microscope to excite the sample and then the PL signals from selected area will be collected be anthor object. After the object, a position-tunabe pin-hole has been placed in the middle of the light path from the object to the spectrometer connected to the streak camera. This pin-hole is the key part to realize the spatial resolution. Because of the diffraction limmit, the object cannot just collect the PL signals only from selective area without the stray light from other area like the excited sopt of the sample. Thus, this position-tunable pinhole is added and calibrated to screen those stray light from unselected area, so that only the PL signals from selected area will be induced into the streak camera.

2. Table S1. Fitted parameters for the in situ-TRPLs and SSTRPLs. Most of passive waveguide can be fitted well by the bi-exponential function. Only one passive PL curve of position 1 can be fitted by mono-exponential function.

The fitting parameters of the in situ-TRPLs and SSTRPLs

	Parameters	P1 (1.93eV)	P2 (1.98eV)	P3 (2.03eV)	P4 (2.11eV)	P5 (2.21eV)
Passive waveguide	τ_1	-	119.6	116.4	101.5	-
	τ_2	809.45	756.3	712.9	364.2	-
	A_1	-	0.55	0.68	0.8	-
	A_2	1	0.45	0.32	0.2	-
Active waveguide	τ_1	-	125.8	97.1	78.4	109.3
	τ_2	-	387.8	365.1	375.6	478.7
	A_1	-	0.6	0.53	0.74	0.8
	A_2	-	0.4	0.47	0.26	0.2
In situ-TRPL	τ_1	150.2	133.8	149.4	74.3	38.2
	τ_2	1052	522.2	445.7	257.4	192.3
	A_1	0.66	0.72	0.79	0.83	0.91
	A_2	0.34	0.28	0.21	0.17	0.09

*Unit of time constants (τ1 and τ2): ps

3. The calculation of the photo-generated carrier density

The initial photo-generated carrier density in the CdS or CdSe nanowire can be calculated by the following equations:[1]

$$N_{photo-generated\ carrier\ density} = \frac{j\sigma}{V} \quad (1)$$

$$\sigma = \frac{\omega}{n_I c}(\pi r^2 l)\left|\frac{4 \in_I}{\in_I + \in_S}\right|^2 (2 n_s k_s) \quad (2)$$

In equation 1, j is the density of photons that goes to the surface of the nanowire in every single pules, V is the volume of excited part of the nanowire, σ is the linear absorption cross section of the NW and can be calculated by equation 2, in which the ω is the angular frequency of the pump photon (400nm, ~4.7 × 1015 s^{-1}), n_I is refractive index of the surrounding medium (air, n_I ~1.0), and $\in_I$ and $\in_S$ are the dielectric constants of the surrounding medium and the nanowire(air, $\in_I$ ~1.0; CdS, $\in_S$=6.18+1.70i; CdSe, $\in_S$=7.9+4i).

In our work, the nanowire is excited by a beam of 400 nm pulsed laser with the frequency of 1kHz which focused into ~500nm, the diameter of the nanowire is about 600 nm and the power density of the laser is 64 μJ/cm^2. So we can estimate the the photo-generated carrier density of CdS nanowire and CdSe nanowire to be 1.18 × 10^{16} cm^{-3} and 1.37 × 10^{16} cm^{-3}, respectively. With the sulfide/selenide ratios of different position on the composition graded NW taken into consideration, the photo-generated carrier density of the position from 1 to 5 on the Figure 1a can be estimated to be 1.24 × 10^{16} cm^{-3}, 1.26 × 10^{16} cm^{-3}, 1.28 × 10^{16} cm^{-3}, 1.29 × 10^{16} cm_{-3}, 1.31 × 10^{16} cm^{-3}, respectively.

4. The PL spectra after active waveguide.

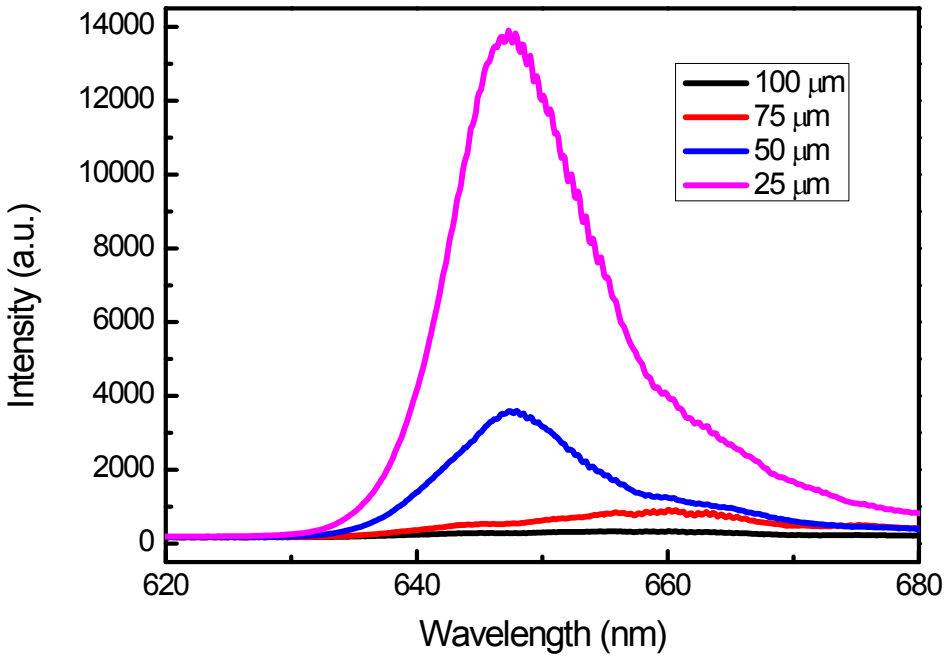

Fig. S2 The PL spectra after active waveguide in different distances. The strength of the PL decreases rapidly with the distance of the active waveguide getting longer.

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5. The theoretical consumption of the light propagation through the composition-graded nanowires by the method of emitting-absorption-reemitting.

The consumption of the propagation of light through the sample can be calculated by the following equations.[2] The intensity of the PL signals propagated through the distance l can be calculated by:

$$I(l) = I_0 e^{-\alpha(h\nu)l} \quad (3)$$

where the I_0 is the initial intensity which is detected at the excited spot of the nanowire, l is the propagation distance and the $\alpha(h\nu)$ is the optical absorption coefficient which is dependent on the photon energy of light emit of the nanowire and because of the composition is continuous changing along the wire, the $\alpha(h\nu)$ is various too. The value of $\alpha(h\nu)$ can be calculated by:

$$For\ E \le E_g(l),\ \alpha(h\nu) = A_0\sqrt{\frac{kT}{2\sigma}}exp\left[\left(\frac{\sigma}{kT}\right)\left(E - E_g(l) - \frac{kT}{2\sigma}\right)\right] \quad (4)$$

$$For\ E > E_g(l),\ \alpha(h\nu) = A_0\sqrt{E - E_g(l)} \quad (5)$$

Among these two equations, the A_0 is the structure-related constant, kT is thermal energy at room temperature and σ is a composition-dependent dimensionless phenomenological fitting parameter. In our sample, the value of σ(WBG) and σ(NBG) is 2.3052 and 2.2106, respectively.

To simulate the method of emitting-absorption-reemitting, we assume the composition-graded nanowire can be divided into n pieces of homogenous parts. In each part, the bandgap $E_g(i)$ and the $\sigma(i)$ can be calculated by the following two equations, respectively.

$$E_g(i) = E_g(0) + \frac{E_g(L) - E_g(0)}{n} i \ (i = 0, 1, 2, ..., n) \quad (6)$$

$$\sigma(i) = \sigma(0) + \frac{\sigma(L) - \sigma(0)}{n} i \ (i = 0, 1, 2, ..., n) \quad (7)$$

where the $E_g(0)$, $E_g(L)$, $\sigma(0)$, $\sigma(L)$ are the bandgap of the excited spot, the bandgap of propagation terminus, the σ of the excited spot and the σ of the propagation terminus, respectively.

Then, consider about the situation of emitting-absorption-reemitting method, the intensity Ii at the propagation terminus can be calculated by:

$$I_i = I_{i-1} e^{-\alpha(h\nu)L/n} (i = 1, 2, ..., n) \quad (8)$$

In our work, the length of the nanowire, L=100 μm, A_0=30000 $cm^{-1}eV^{-1/2}$, kT=25 meV and n=100.

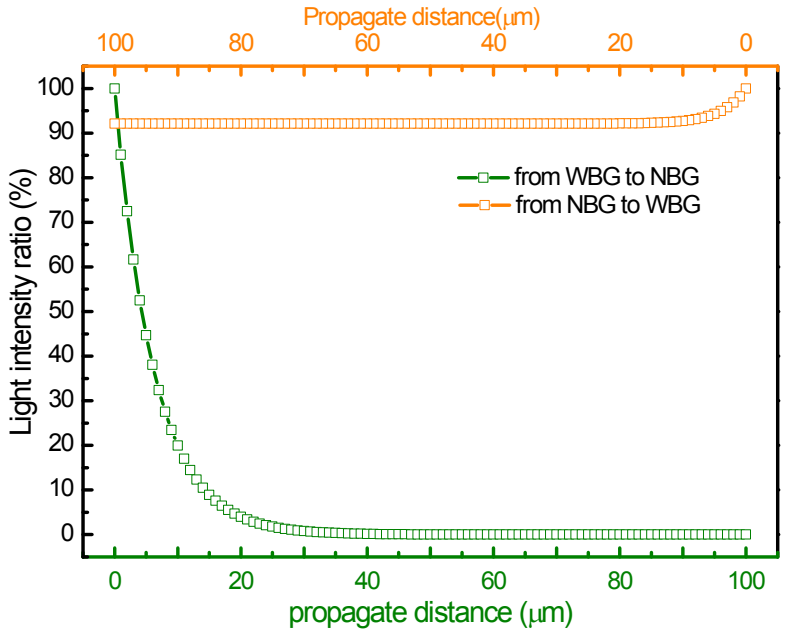

Fig. S3 The theoretical light intensity ratio trace of different propagation direction along the composition-graded nanowire.

With the bandgap of the excited spot and propagation terminus considered, the ratio of the intensity after the transport by the method of emitting-absorption-reemitting was calculated and the plotted in the Fig. S2.

6. Quantum Yield Measurements.

Carboxylate-modified microspheres (Fluo Sphere, type F8816, d=1μm, λ_{em}=645 nm, Relative quantum yield QYR~18%) were supplied as a quantum yield reference in this experiment.[3] To measure single microsphere emission, we diluted the microsphere solution and then dispersed it to a substrate to get monodisperse microsphere. A CW laser at 532 nm was used to excited single microsphere and the sample under laser power of ~50 nW. The emitted light was collected by an objective lens (Zeiss, ×100, N.A.~0.9) and detected by a spectrometer (WITec, UHTS 300 SMFC). The integrated emission intensity counts IR (IS) for single microsphere (NW sample) were obtained. The quantum yield of a sample (QYs) can be calculated by using the following equation, QYs=(IS/IR)×QYR. The QY of the single NW is estimate to be around 0.5%-1% from $CdS_{0.75}Se_{0.25}$ to $CdS_{0.38}Se_{0.62}$.

Notes and references

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2. J. Xu, X. Zhuang, P. Guo, W. Huang, W. Hu, Q. Zhang, Q. Wan, X. Zhu, Z. Yang, L. Tong, X. Duan and A. Pan, Scientific Reports, 2012, 2.
3. F. Vietmeyer, P. A. Frantsuzov, B. Janko and M. Kuno, Physical Review B, 2011, 83, 10.