

Supporting Information

Optically-Controlled Quantum Size Effect in a Hybrid Nanocavity Composed of a Perovskite Nanoparticle and a Thin Gold Film

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S1. Crystalline structures of CsPbBr₃ nanoparticles before and after the phase transition

The crystalline structures of CsPbBr₃ nanoparticles before and after the phase transition were characterized by using high resolution transmission electron microscopy (HR-TEM). A typical example is shown in Figure S1. It can be seen that the CsPbBr₃ nanoparticle is initially composed of a large number of quantum dots with a feature size of ~5.0 nm. It can be considered as a polycrystalline nanoparticle which exhibits optical properties similar to single quantum dots, such as the quantum size effect. After the phase transition, the monocrystalline nanoparticle is obtained with a lattice constant of ~0.29 nm. As a result, the quantum size effect, which is generally manifested in the emission wavelength, disappears completely.

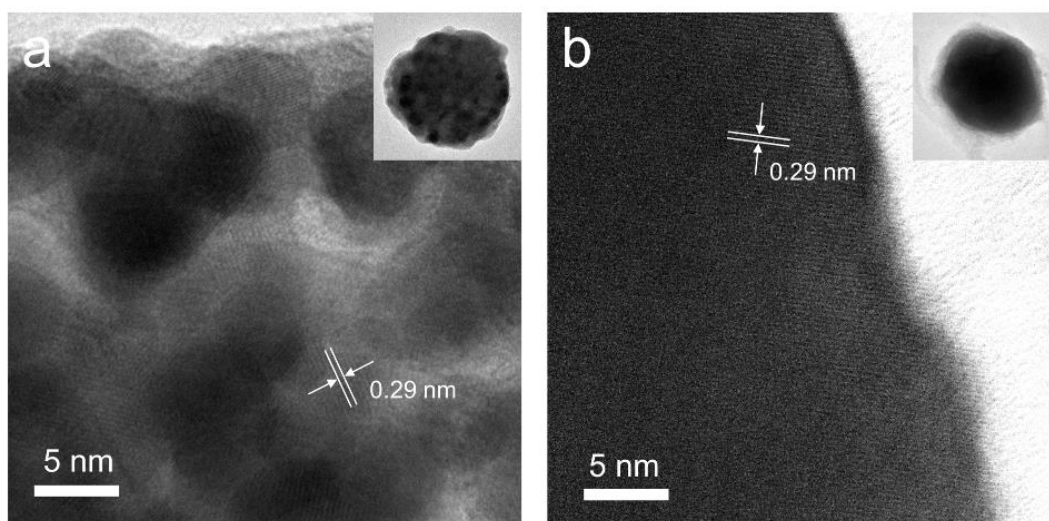


Figure S1 HR-TEM images of a CsPbBr₃ nanoparticle before a) and after b) the phase transition. The images of the whole nanoparticles are shown in the insets.

S2. PL spectra of CsPbBr₃ nanoparticles after phase transition

We also measured the photoluminescence (PL) spectra for CsPbBr₃ nanoparticles after the polycrystalline to monocrystalline phase transition at different excitation laser powers. A typical example is shown in Figure S2. A slope of ~2.1 is derived from the dependence of the PL intensity on the laser power, which is plotted in a logarithmic coordinate (see the inset). It implies that the PL is mainly caused by two-photon-induced absorption (TPA) process.

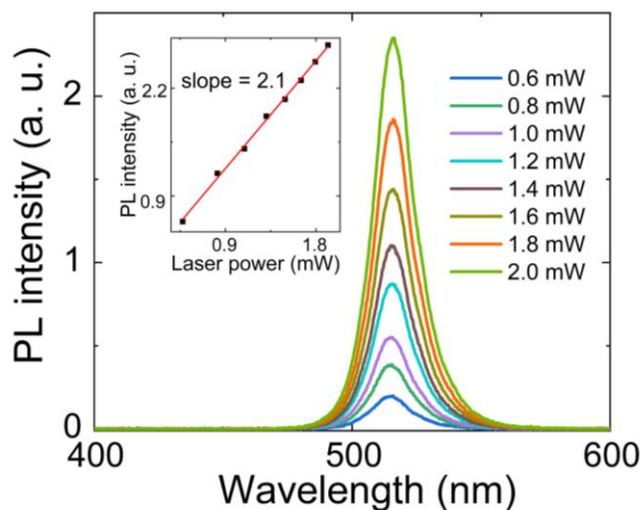


Figure S2 PL spectra measured for a CsPbBr₃ nanoparticle after the phase transition at different excitation laser powers. The dependence of the PL intensity on the excitation laser power is shown in the inset.

S3. Optical properties of CsPbBr₃ nanoparticles placed on a SiO₂ substrate

For comparison, we also examined the backward scattering spectra of CsPbBr₃ nanoparticles with different diameters placed on a SiO₂ substrate, as shown in Figure S3a-c. From the $[\int |E(\lambda)|^2 dV]/V$ and $[\int |E(\lambda)|^4 dV]/V$ spectra, it can be seen that the emission and excitation efficiencies of the CsPbBr₃ nanoparticles on the SiO₂ substrate are significantly reduced as compared with those on the Au/SiO₂ substrate. More importantly, spatially-localized temperature distribution is not available for the CsPbBr₃ nanoparticles on the SiO₂ substrate. Therefore, optically-controlled quantum size effect cannot be realized by using such CsPbBr₃ nanoparticles. In Figure S3d, we present the photoluminescence (PL) spectra of a CsPbBr₃ nanoparticle on the SiO₂ substrate excited by using 800-nm femtosecond laser pulses with a low repetition rate of 3.8 MHz at different average powers. Different from the CsPbBr₃ nanoparticles on the Au/SiO₂ substrate, only a single emission peak is observed in the PL spectrum. It implies that the phase transition is completed in a short time, which is in good agreement with the prediction of the calculated transient temperature distribution (Figure 3d).

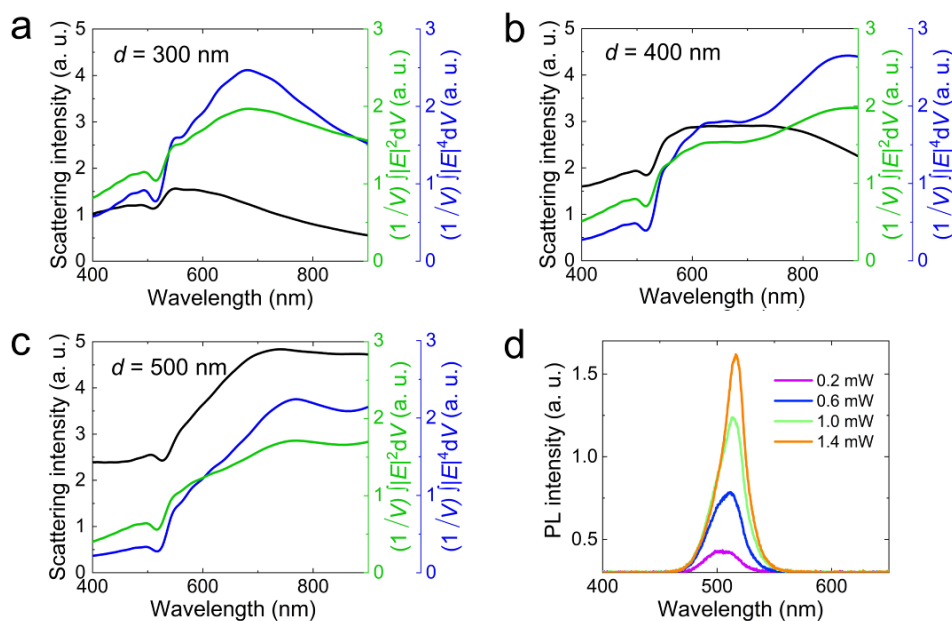


Figure S3 a)-c) Backward scattering spectra calculated for CsPbBr₃ nanoparticles with different diameters of 300, 400 and 500 nm placed on a SiO₂ substrate. d) PL spectra measured for a CsPbBr₃ nanoparticle placed on a SiO₂ substrate at different laser powers, which is excited by using 800-nm femtosecond laser pulses with a low repetition rate of 3.8 MHz.

S4. Electric and magnetic field distributions in the hybrid nanocavity

In order to gain a deep insight into the optical modes supported by the hybrid nanocavity, we calculated the electric and magnetic field distributions in the XY plane for the hybrid nanocavity composed of a CsPbBr₃ nanoparticle with $d = 400$ nm at the excitation and emission wavelengths (800 and 515 nm), as shown in Figure S4a-d. It is noticed that the largest electric field is achieved in the gap region between the nanoparticle and the Au film.

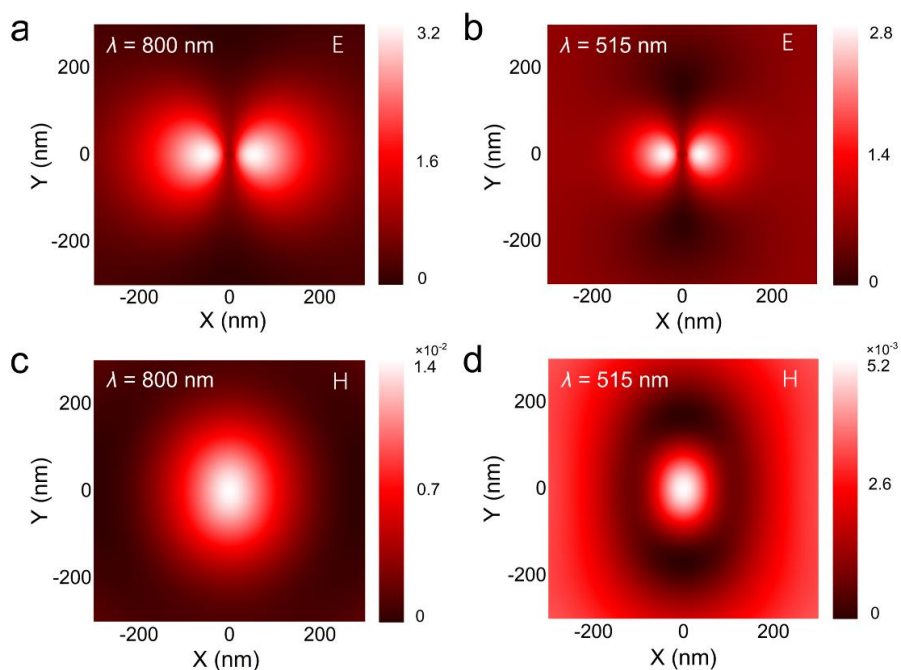


Figure S4 Electric field distributions in the XY plane calculated for the hybrid nanocavity composed of a CsPbBr₃ nanoparticle with $d = 400$ nm at 800 nm a) and 515 nm b). The corresponding magnetic field distributions are shown in c) and d), respectively.

S5. Broadband emission from the hybrid nanocavity

The emission property of the hybrid nanocavity can also be manipulated by further lowering the repetition rate from 3.8 to 2.9 MHz. In [Figure S5](#), we show the evolution of the PL spectrum of a hybrid nanocavity with increasing laser power, which is excited by using 800-nm femtosecond laser pulses with a repetition rate of 2.9 MHz. Instead of two distinct emission peaks which is generally observed for hybrid nanocavities excited by using 800-nm femtosecond laser pulses with a repetition rate of 3.8 MHz, one can see a broadband emission below the threshold for the phase transition. A single and narrow peak is observed in the PL spectrum after the phase transition is completed above the threshold.

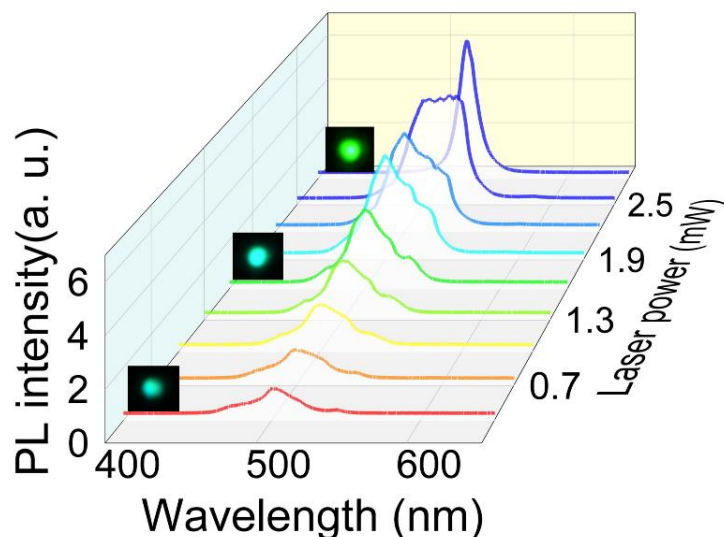


Figure S5 Evolution of the PL spectrum of the hybrid nanocavity excited by using 800-nm femtosecond laser pulses with a repetition rate of 2.9 MHz.

S6. Phase transition induced by irradiating femtosecond laser pulses

Although reversible phase transition can be realized by using femtosecond laser pulse with a low repetition rate of 3.8 MHz, the phase transition from polycrystalline to monocrystalline can still be induced in a CsPbBr₃ nanoparticle if the laser power exceeds a critical value because of the heat accumulation effect. In [Figure S6](#), we show the temporal evolution of the PL spectrum of a hybrid nanocavity excited by using femtosecond laser pulse with a repetition rate of 3.8 MHz and an average power of 2.4 mW, which is above the threshold for the phase transition (~2.0 mW). It can be seen that the PL spectrum is initially dominated by the emission at ~488 nm. With increasing irradiation time, it gradually becomes dominated by the emission at ~520 nm. After about one minute, only a single emission peak at ~515 nm is observed.

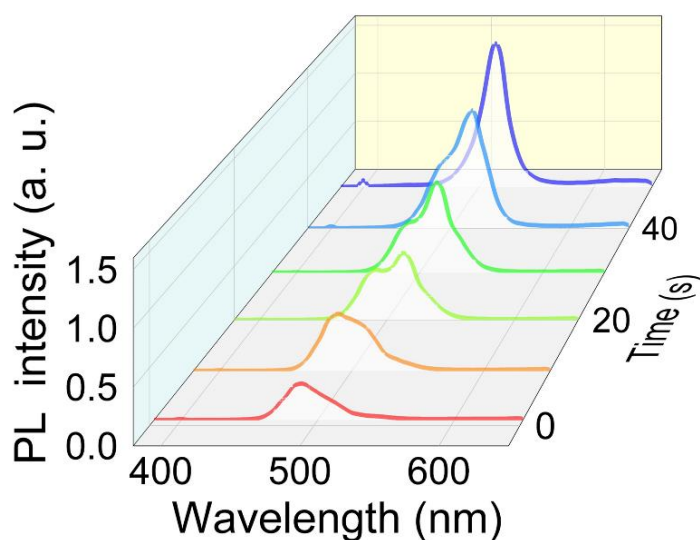


Figure S6 Temporal evolution of the PL spectrum of a hybrid nanocavity excited by using 800-nm femtosecond laser pulses with a repetition rate of 3.8 MHz and an average power of 2.4 mW.

S7. Forward scattering spectra from the hybrid nanocavity

The excitation power is lower than the threshold for the phase transition, dual-wavelength emission with equal intensities at the two wavelengths can be realized. In [Figure S7](#), we present the forward scattering spectra of the nanoparticles measured at different times. No obvious change is found, implying the crystalline structure is quite stable.

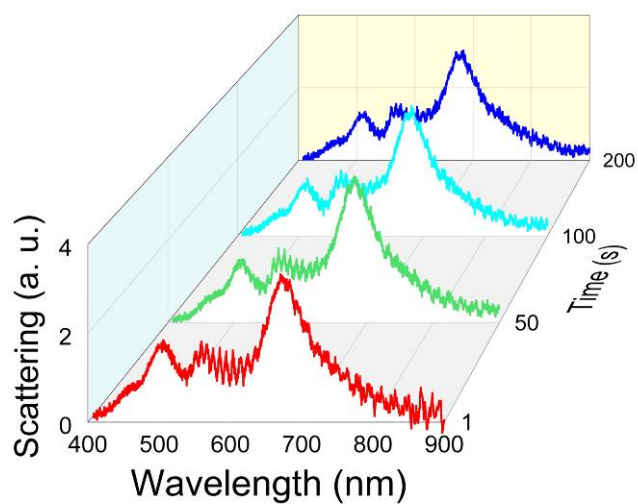


Figure S7 Forward scattering spectra of the hybrid nanocavity measured at different times.