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Supporting Information for

Strong plasmon-exciton coupling in colloidal halide perovskite nanocrystals near a metal film

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Table of Contents:

Experimental Methods and Theoretical Calculations

Materials. Lead(II) iodide (PbI_2, 99%), Cesium acetate ($C_2H_3CsO_2$, 99.99%, Sigma-Aldrich), Cesium carbonate (Cs_2CO_3, 99.9%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), oleylamine (OLAM, 70%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Toluene (≥99%, Merck) was purchased and used without any further purification.

Synthesis of Cs-Oleate for Nanowires. In a standard synthesis of Cs-oleate, 81.4 mg of Cs_2CO_3, 4 mL of ODE, and 1.25 mL of OA were loaded in a glass tube and dried under vacuum for 1 h at 120 ºC. After degassing, the temperature was increased to 150 °C under the flow of nitrogen gas and then Cs-oleate was obtained after 2 h. Before its use in the synthesis of $CsPbI_3$, Cs-oleate solution was heated to 100 ºC in order to completely dissolve Cs-oleate in ODE.

Synthesis of Cs-Oleate for Nanoplatelets. Briefly, 96 mg of Cesium acetate was dissolved in 10 mL of OA under ultrasonication until a clear solution was obtained. The final solution was stored in the ambient condition for further use.

$CsPbI_3$ nanoplatelet synthesis. $CsPbI_3$ NPLs were synthesized by using a previously described route by Huang et al.[1] Briefly, 0.1 mmol of PbI_2 powder was completely dissolved in 100 µL of OA, 100 µL of OLAM, and 10 mL of toluene mixture at 80 ºC under continuous stirring. Subsequently, 2 mL of PbI_2 precursor solution was added in a glass vial under vigorous stirring at room temperature. Finally, 50 µL of Cs-Oleate (for nanoplatelets) solution was quickly injected into the above solution combination and after, 2 minutes, the solution was centrifuged at 14500 rpm for 5 minutes. The obtained precipitate was dispersed in toluene.

$CsPb(Br/I)_3$ nanoplatelet synthesis. $CsPb(Br/I)_3$ NPLs were synthesized by using the same procedure, which was described above. In order to synthesize $CsPb(Br/I)_3$ NPLs, PbI_2 and $PbBr_2$ precursor solution mixtures were used with different amounts for tuning the optical properties of the nanoplatelets. The $PbBr_2$ precursor solution was prepared in a similar to that

of PbI_2 precursor solution. During the precursor solution preparation, instead of 0.1 mmol of PbI_2 powder, 0.1 mmol of $PbBr_2$ powder was used.

$CsPbI_3$ nanowire synthesis. $CsPbI_3$ nanowires were synthesized by using a solvothermal process. Firstly, 230.5 mg of PbI_2 was dissolved in 5 mL of ODE, 1 mL of OA and, 1 mL of OLAM mixture at 120 ºC under ambient condition. After the complete dissolution, the solution was cooled down to room temperature. Afterwards, 600 µL of Cs-Oleate, which was preheated to 100 ºC, was added to the PbI_2 precursor solution under continuous stirring. The prepared solution was loaded into the Teflon lined autoclave, and then the autoclave was sealed and placed into the preheated oven at 150 ºC for an hour. The nanowire colloid was quenched by immersing in an ice bath and then centrifuged for 10 min at 6000 rpm. The NCs were dispersed in toluene and stored at ambient atmosphere.

Characterization of Nanocrystals. Scanning Transmission Electron Microscopy (STEM) analysis of pure and doped samples was carried out in order to observe morphology of the nanocrystals (SEM; Quanta 250, FEI, Hillsboro, OR, USA). The samples were prepared by drop-casting diluted NC suspensions onto 200 mesh carbon-coated copper grids. Absorption (Abs), Photoluminescence (PL), and time-resolved lifetime (LT) measurements were carried out by using a FS5 Spectrofluorometer (Edinburgh Instruments, UK). Samples were diluted in toluene and the optical properties of the NCs were measured in a cylindrical quartz cuvette. For LT measurements of the samples, the samples were excited with a 450 nm laser with a pulse width of 100 ps and a repetition rate of 1 MHz.

Plasmon-exciton coupling. A well-known Kretschmann configuration was used in order to study strong coupling of perovskite excitons with surface plasmon polaritons (SPPs) of metal thin films.[2] SPPs can be excited by using a prism in the Kretschmann configuration or a metal film coated dielectric diffraction grating.[3] Firstly, a glass substrates were cleaned with a piranha solution, a 3:1 mixture of sulfuric acid (95%) and hydrogen peroxide (30%), and then coated

with 40 nm thick Ag film fabricated by thermal evaporation of Ag under vacuum. Silver thin films were then inserted into a solution of 10 ml of 10 mM 16-mercaptohexadecanoic acid (90%) in isopropanol for 30 minutes and subsequently the substrates were washed with isopropanol. Afterwards, the nanocrystals were spin coated on the silver substrates. A tunable laser light source having a spectral width of around 1 nm (Koheras-SuperK Versa) and connected to an acousto-optic tunable filter working in the visible and near infrared region of the electromagnetic spectrum was used in order to obtain dispersion curves of the perovskite NCs on the silver film.

Theoretical calculations. The finite difference time domain (FDTD) method was employed to calculate optical properties of coupled perovskite NCs placed on flat Ag films. In theoretical calculations, the plane wave moves in the z-axis and the mesh size is 1 nm during polariton dispersion curve calculations. The electric field polarization is p-polarized in order to couple incident light to surface plasmons on the flat metal film. A glass prism was used to couple incident light to surface plasmons of metal film. The excitonic modes of the perovskite NCs were assumed to be Lorentzian and expressed as $\varepsilon(\omega) = \varepsilon_\infty + f_0(\omega_0^2/(\omega_0^2-\omega^2-i\gamma_0\omega))$ where the resonance wavelength of the oscillator and the width of the plasmon resonance (γ_0) were adjusted for each perovskite NCs. The background index was taken as 2.1. The perovskite plexciton dispersion curves were generated by acquiring the reflection spectra for each incidence angle within a broad wavelength range and then the resulting reflectivity distribution for each incidence angle was obtained in a heat map.

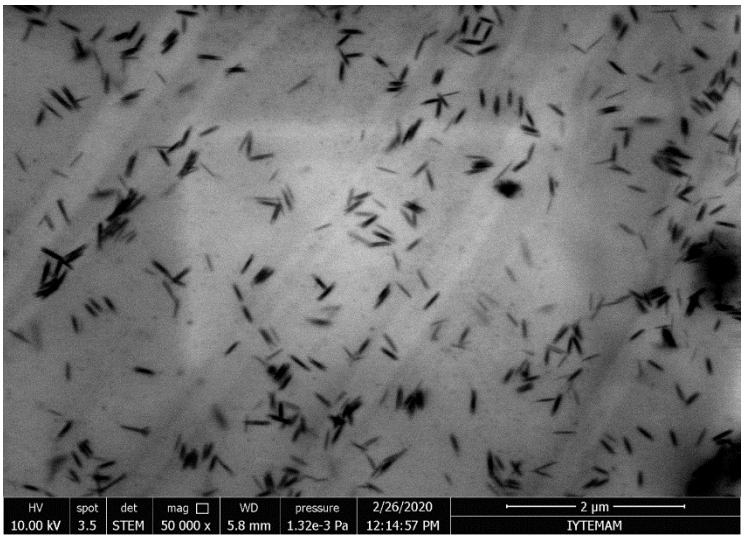

Fig. S1 Large area STEM image of halide perovskite nanoplatelets.

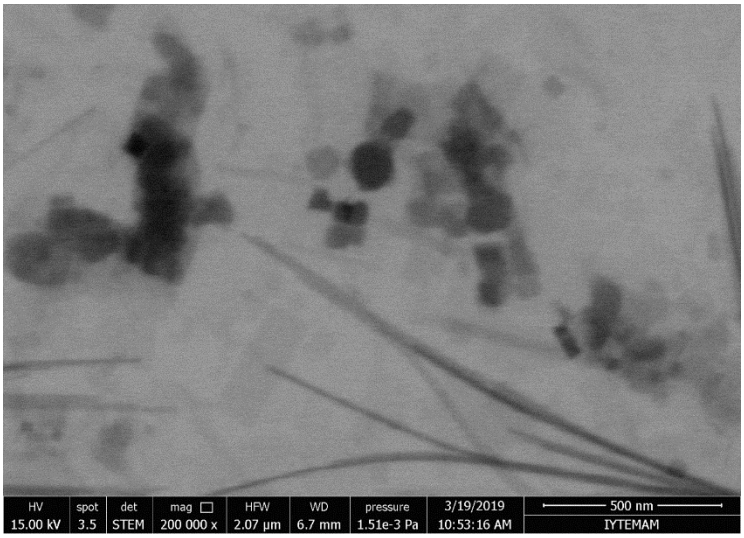

Fig. S2 STEM image of halide perovskite nanowires. There are also a few halide perovskite nanocubes in the image.

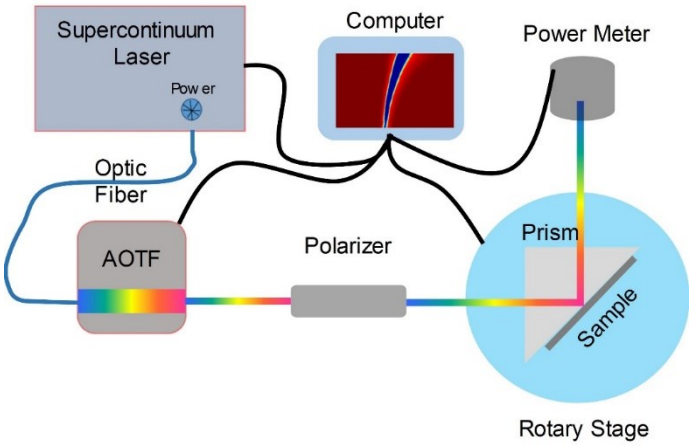

Fig. S3 Schematic representation of the experimental set up used to investigate coupling of excitons of perovskite quantum dots and propagating surface plasmon polaritons of silver film in the visible spectrum. The dispersion curves were generated by using a a tunable laser light source with a spectral width of around 1 nm; i.e., supercontinuum laser (Koheras-SuperK Versa) with acousto-optic tunable filter working in the visible and near infrared. The rotary stage controls incidence angle of the incoming light. The polarization of the incident light is p-polarized. The power meter measures the power of the reflected light for each wavelength of the reflected light. The reflected light is normalized with the s-polarized light and hence the reflected light intensity gives specific information about the coupling of incident light to surface plasmons. Note that, in the strong coupling regime, incident light is coupled to surface plasmons on thin metal films and therefore surface plasmon polaritons are generated. The SPPs are further coupled with excitons in the strong coupling regime and mixed plasmon-exciton polaritons are formed.[4] In this study, the perovskite plexciton polaritons have been demonstrated both theoretically and experimentally in the polariton dispersion curves.

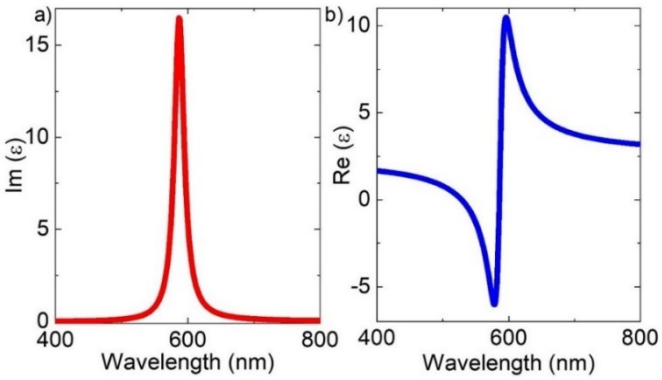

Fig. S4 (a) Imaginary (b) real parts of the dielectric function of Lorentz Oscillator used for modeling perovskite quantum dots placed in close proximity of a thin metal film in FDTD simulations.

Table S1. Obtained PL lifetime data of perovskite quantum dots from biexponential, and triexponential fits, and their average lifetimes.

	τ_1(ns)	τ_2(ns)	τ_3(ns)	f_1(%)	f_2(%)	f_3(%)	τ_{avg}(ns)
CsPbI3 NW	6.4005	55.8105	-	6.21	93.79	-	55.4381
CsPbI3 NPL	10.5930	24.6461	-	44.88	55.12	-	21.0030
CsPb(Br/I)3 NPL	1.4113	4.6667	13.2445	8.37	68.50	23.13	8.7262

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