

Metal-enhanced Photoluminescence in Perovskite Quantum Dots-hBN-Gold Film Mixed-dimensional Van der Waals Heterostructure

*Kunjie Zhou^{1 §}, Jingyi Zhu^{1 §}, Ruisi Meng^{2 §}, Wei Zeng¹, Zhuo Xue¹, Chen Shen¹, Yueran Zhao³,
Yuchen Zhou², Mengyao Li², Yanan Wang², Kenji Watanabe⁴, Takashi Taniguchi⁵, Minliang
Lai^{3*}, Jia Lin^{2*}, and Sheng Wang^{1,6*}*

1 Key Laboratory of Artificial Micro-and Nano-structures of Ministry of Education, and School
of Physics and Technology, Wuhan University, Wuhan, Hubei 430072, China

2 Department of Physics, Shanghai University of Electric Power, Shanghai 200090, China

3 School of Nano Science and Technology, Suzhou Institute for Advanced Research, University
of Science and Technology of China, Suzhou, Jiangsu 215123, China

4 Research Center for Electronic and Optical Materials, National Institute for Materials Science,
1-1 Namiki, Tsukuba 305-0044, Japan

5 Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1
Namiki, Tsukuba 305-0044, Japan

6 Wuhan Institute of Quantum Technology, Wuhan, Hubei 430206, China

*Email: mllai@ustc.edu.cn, jlin@shiep.edu.cn, shengwang16@whu.edu.cn

ABSTRACT

All-inorganic cesium lead halide perovskite quantum dots (QDs) have emerged as promising materials for next-generation optoelectronic devices due to their exceptional photoluminescence (PL) properties, including high quantum yields and narrow emission linewidths. However, unlocking their full potential requires innovative strategies to further enhance and precisely tune their fluorescence efficiency. In this work, we present a novel 0D-2D-3D mixed-dimensional van der Waals (vdW) heterostructure comprising CsPbBr₃ QDs, multilayer hexagonal boron nitride (hBN), and a gold (Au) nanoparticle film, achieving a remarkable 7-fold PL enhancement. We attribute this enhancement to the synergy of plasmon-induced enhancement of the incident electromagnetic field and an increased spontaneous emission rate via the Purcell effect, optimized by tuning the hBN spacer thickness to 26 nm. This heterostructure design provides new insights into metal-enhanced photoluminescence for perovskite quantum dots, and it offers a scalable platform to enhance efficiency in future optoelectronic applications.

KEYWORDS: perovskite quantum dots, metal-enhanced photoluminescence, mixed-dimensional vdW heterostructure, surface plasmons, Purcell effect

INTRODUCTION

All-inorganic halide perovskite quantum dots (QDs), exemplified by CsPbBr₃ QDs, have garnered widespread attention in photonics and optoelectronics, due to their high quantum yields, narrow emission linewidths, and composition-tunable optical properties. These attributes make them ideal candidates for applications in light-emitting diodes (LEDs), solar cells, photodetectors, and quantum light sources.^{1–14} Despite significant progress in optimizing perovskite QD fluorescence through surface passivation, size engineering, and ligand exchange,^{15–19} their performance remains constrained by factors such as nonradiative recombination and environmental instability, necessitating novel enhancement strategies.

Plasmonic nanostructures offer a powerful approach to boost the fluorescence of emitters by leveraging surface plasmons—collective oscillations of free electrons at metal-dielectric interfaces.^{20–31} When fluorophores are positioned near plasmonic surfaces, the local electromagnetic field is enhanced, and the radiative decay rate is amplified via the Purcell effect, increasing quantum yield.^{32,33} This metal-enhanced PL technique has proven effective for diverse materials, including transition metal dichalcogenides (TMDs), organic dyes, and semiconductor nanocrystals,^{34–39} yet its application to Perovskite QDs remains underexplored.

Concurrently, mixed-dimensional van der Waals (vdW) heterostructures—combining materials of different dimensionalities (e.g., 0D quantum dots, 2D layers, and 3D films)—have emerged as a versatile platform for tailoring optoelectronic properties, thanks to their atomically sharp interfaces and tunable band alignments.^{40–45} These systems enable precise control over light-matter interactions, making them ideal for integrating plasmonic enhancements with Perovskite QDs. Moreover, as an insulating 2D crystal, hexagonal boron nitride (hBN) features an atomically smooth surface with minimal dangling bonds and charged impurities, and its layered hexagonal

lattice structure with strong in-plane ionic bonding ensures chemical inertness and stability while maintaining excellent insulating properties even at monolayer thicknesses.^{41,46} These exceptional dielectric characteristics of hBN render it an ideal candidate for engineering van der Waals heterostructures and fabricating high-performance optoelectronic devices.

In this study, we introduce a pioneering 0D-2D-3D mixed-dimensional vdW heterostructure composed of 0D semiconducting CsPbBr₃ QDs, 2D insulating multilayer hBN, and 3D conducting gold (Au) nanoparticle film. This unique architecture, enabled by the 2D nature of hBN, allows for precise tuning of the PL emission of CsPbBr₃ QDs by varying the thickness of the hBN spacer. We achieved a maximum PL enhancement of 7-fold at an hBN thickness of 26 nm with reduced PL lifetime, revealed by confocal scanning PL microscopy and fluorescence lifetime imaging microscopy (FLIM). Theoretical analysis and numerical simulations further corroborate the experimental observations, showing that both the plasmon-induced enhancement of the excitation field and the Purcell effect contribute to the observed PL enhancement. This work offers a scalable strategy for optimizing perovskite-based devices, including high-efficiency perovskite quantum dot light-emitting diodes (PeLEDs), photodetectors, and phototransistors,^{47–49} while laying the groundwork for the future development of mixed-dimensional vdW heterostructures in advanced optoelectronics.

RESULTS AND DISCUSSION

QDs Synthesis and Heterostructure Fabrication

We synthesized CsPbBr₃ QDs using a hot-injection method, as detailed in the Supporting Information.⁵⁴ Transmission electron microscopy (TEM) analysis (Figure 1a) revealed that the QDs exhibited a cubic morphology with an average size of 9.9 nm and a size dispersion of 13%. High-resolution TEM imaging (inset, Figure 1a) further confirmed the uniformity and single-

crystalline nature of the nanoparticles. Given that the Bohr diameter for Wannier-Mott excitons in CsPbBr₃ is approximately 7 nm,^{1,14} our QDs, with dimensions comparable to this characteristic length scale, are expected to exhibit quantum confinement effects. The PL spectrum of CsPbBr₃ QDs dispersed in hexane at room temperature (Figure 1c) shows an emission peak at around 510 nm (~2.43 eV). To determine the exciton binding energy and continuum transition bandgap in CsPbBr₃ QDs, we performed a systematic analysis of the ultraviolet-visible (UV-vis) absorption spectrum at room temperature (Figure 1c), which exhibits a steep absorption edge followed by a plateau regime. The absorption spectrum was fitted using the well-known Elliott formula,^{50–52} with representative fitting results presented in Figure S1, and this analysis reveals distinct spectral contributions from both discrete excitonic states and continuum transitions. The fitting results yield a continuum transition bandgap (E_g) of 2.496 eV and an exciton binding energy (E_b) of 34 meV, and the associated excitonic transition displays a full width at half maximum (FWHM) of 88 meV, showing close consistency with reported values for CsPbBr₃ quantum dots.^{1,53} Detailed spectral fitting method and corresponding fitting parameters are provided in the Simulation Section and Table S1 in the Supporting Information, respectively. In addition, the photoluminescence quantum yield (PLQY) of the colloidal QD solution was measured to be 45.1% under 365 nm excitation at an intensity of 0.12 mW/cm² (see Figure S2).

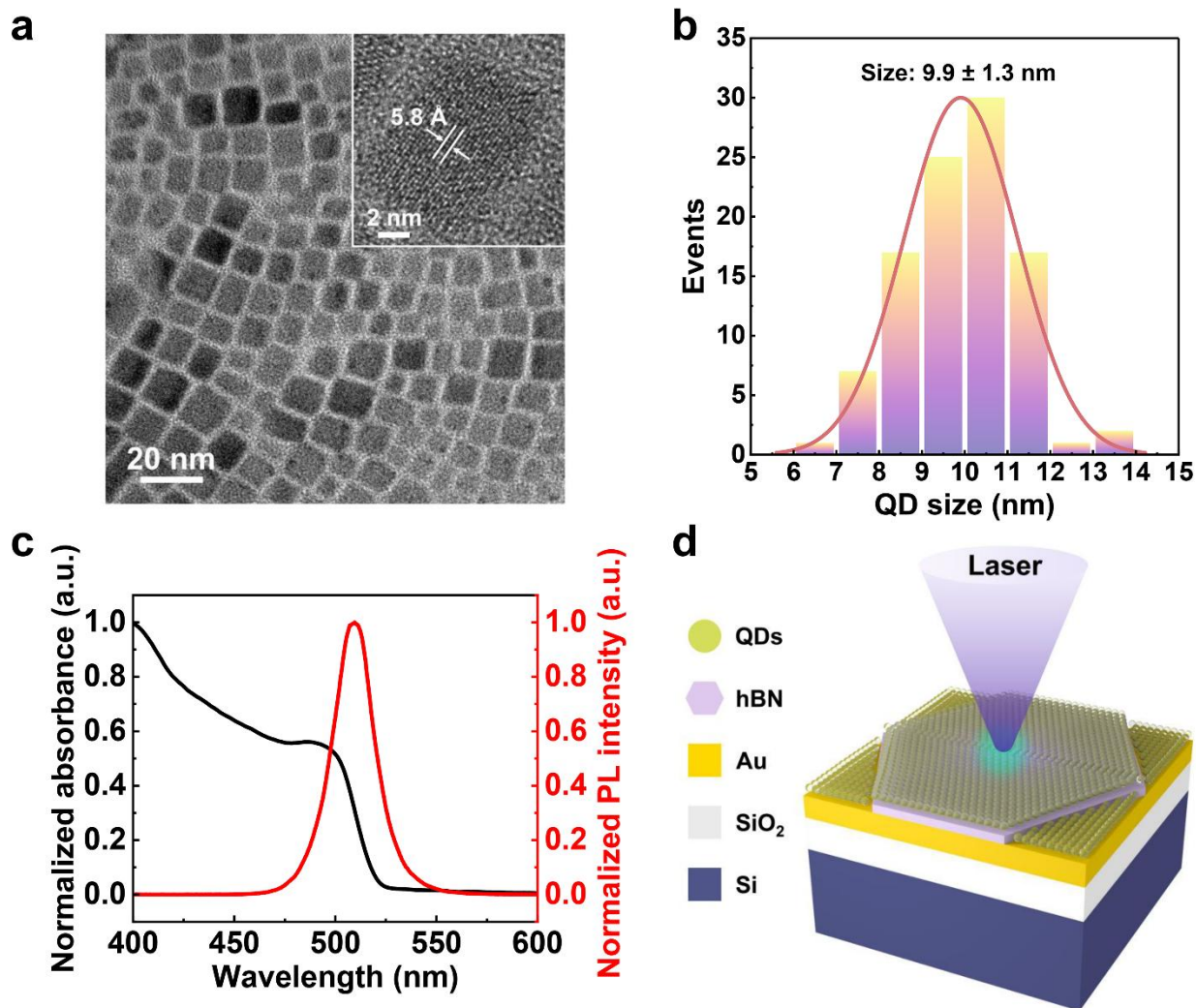


Figure 1. Structural and optical characterization of CsPbBr₃ QDs and schematic of the mixed-dimensional heterostructure. (a) TEM image of CsPbBr₃ QDs displaying cubic morphology with an average size of 9.9 nm. The inset shows a high-resolution TEM image highlighting crystallinity. (b) Size distribution histogram of CsPbBr₃ QDs derived from TEM, fitted with a Gaussian curve (red line). (c) UV-vis absorption (black) and PL (red) spectra of CsPbBr₃ QDs in hexane at room temperature. (d) Schematic illustration of the 0D-2D-3D mixed-dimensional vdW heterostructure.

The schematic in Figure 1d illustrates the configuration of our experimental 0D-2D-3D mixed-dimensional van der Waals (vdW) heterostructure. This structure consists of a 0D CsPbBr₃

QD nanolayer positioned above a 3D gold (Au) nanoparticle film, with a mechanically exfoliated hBN layer acting as a 2D dielectric spacer to mitigate quenching effects. The fabrication process began with the deposition of a 60 nm thick Au film onto a 90 nm SiO₂/Si substrate via thermal evaporation. Subsequently, multilayer hBN was exfoliated from bulk crystals onto a polydimethylsiloxane (PDMS) stamp and transferred onto the Au film. The thickness of the hBN layer was initially estimated using optical color contrast and later confirmed through atomic force microscopy (AFM) measurements. To form the CsPbBr₃ QD nanolayer, we diluted the colloidal QD solution to an appropriate concentration and spin-coated 40 μ L of the solution onto the pre-fabricated hBN-Au-SiO₂/Si structure at 3000 rpm for 60 s. As a control, CsPbBr₃ QDs were also spin-coated onto bare SiO₂/Si substrates for comparison.

To validate the uniformity of the fabricated heterostructure samples presented in Figure 1d, we performed AFM measurements for a representative CsPbBr₃ quantum dots-hBN-gold heterostructure, with the results presented in Figure S3. Figure S3a displays the topographic image of the heterostructure over a $50 \times 50 \mu\text{m}^2$ area. Figures S3b and S3c show $5 \times 5 \mu\text{m}^2$ magnified views of the quantum dots on 131 nm and 11 nm hBN layers, corresponding to the regions marked by Box 1 and Box 2 in Figure S3a, respectively. The distribution density of CsPbBr₃ individual dots or small clusters is $\sim 10/\mu\text{m}^2$ extracted from AFM measurements. These images demonstrate that, since the light spot diameter (exceeding 1 μm) in our optical measurements results in statistically averaged signals over a small area, the quantum dots within the optical measurement regime can be considered as being deposited on the hBN platform with relative uniformity in a dispersed manner.

In addition, to evaluate the air stability of our spin-coated CsPbBr₃ QD layers, we monitored the temporal evolution of PL spectra from the same area of the QD layer over 120 minutes of air

exposure, as presented in Figure S4. The results demonstrate a mere 4.4% reduction in PL intensity while maintaining invariant spectral line shape compared to the initial measurement, indicating robust moisture and oxygen stability of our QDs after removal from the hexane solution. Considering that subsequent photoluminescence and time-resolved photoluminescence characterization were conducted under ambient conditions, this observed stability confirms that the optical properties of the quantum dots remain effectively preserved without significant degradation throughout the experimental testing period.

Optical Characterization and PL Enhancement

Figure 2a presents the optical image of a representative heterostructure sample fabricated in our experiment. Due to their nanoscale dimensions, the CsPbBr₃ QDs deposited on the surface are not visible under an optical microscope, as their size is below the diffraction-limited spatial resolution. However, in the corresponding atomic force microscopy (AFM) image (Figure 2b) of the same region as outlined in Figure 2a, the presence of CsPbBr₃ QDs is clearly distinguishable on both the hBN and Au substrates. To investigate the surface plasmon-induced PL enhancement and its dynamics, we employed confocal scanning PL microscopy (405 nm, 10 W/cm² excitation) and FLIM (375 nm, 10 W/cm² excitation) on the same region, as shown in Figures 2c and 2d, respectively.⁵⁵ In addition, we present another representative smaller-scale heterostructure in the Supporting Information, with corresponding optical, confocal scanning PL, and FLIM images displayed in Figure S5a, b, and c, respectively. This heterostructure consists of hBN with a thickness of approximately 20 nm and dimensions of $\sim 80\ \mu\text{m} \times 30\ \mu\text{m}$, thus allowing the complete architecture to be clearly and entirely visualized across all panels of Figure S5.

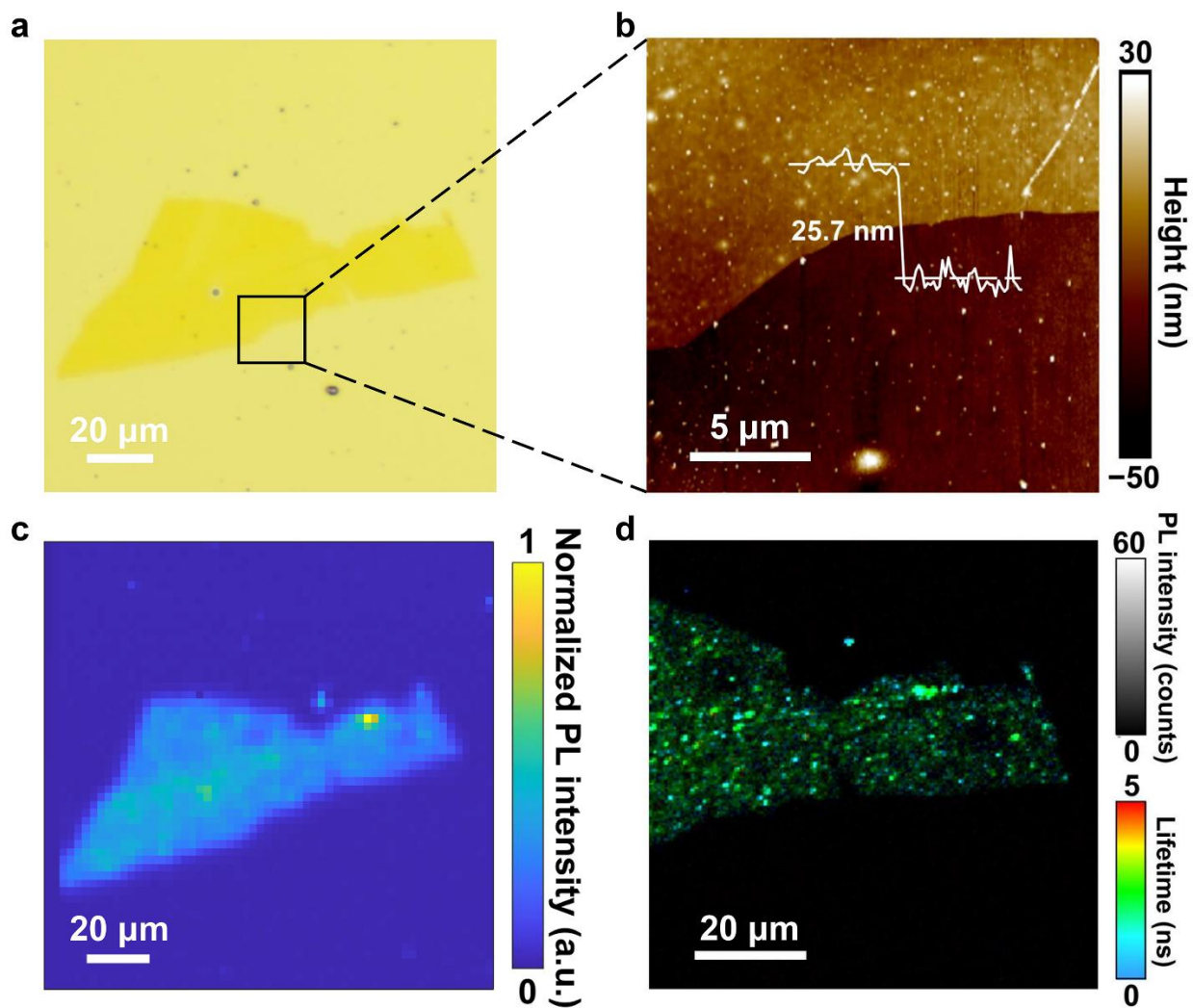


Figure 2. Optical characterization of a representative CsPbBr₃-hBN-Au mixed-dimensional heterostructure. (a) Optical microscopy image of the heterostructure. (b) AFM image of the region outlined in (a). The inset shows a height profile. (c) Confocal scanning PL image of the same region as (a) under continuous 405 nm excitation at an intensity of 10 W/cm². (d) FLIM image of the same region as (a) under pulsed 375 nm excitation at an intensity of 10 W/cm².

As illustrated in Figures 2c and 2d, the fluorescence intensity of CsPbBr₃ QDs is significantly enhanced when placed on the hBN spacer, whereas it is notably suppressed on the Au substrate. Furthermore, the fluorescence lifetime map reveals that the PL lifetime of QDs varies significantly

across different substrates (Figure 2d), indicating the modulation of the PL lifetime by the heterostructure.

Figure 3a presents the PL spectra of CsPbBr₃ QDs deposited on the hBN/Au heterostructure with varying hBN thicknesses, ranging from 5 to 100 nm. For comparison, Figure S6 displays the PL spectra of QDs on the optimized heterostructure (with 26 nm thick hBN) alongside those on a bare SiO₂/Si substrate. The results indicate a substantial enhancement in PL intensity for QDs on hBN, with the emission peak centered around 518 nm. A slight variation in peak position is observed across different spectra, which we attribute to minor differences in QD size at different locations.

To quantify the enhancement, we define the fluorescence enhancement factor, $f = \frac{I_0}{I}$, where I represents the PL intensity of CsPbBr₃ QDs on the hBN/Au heterostructure, and I_0 corresponds to the PL intensity of the same emitters on the SiO₂/Si control substrate. We extracted the enhancement factor from confocal scanning PL measurements, averaging the PL intensities over regions with the same hBN thickness to minimize errors due to potential inhomogeneities in QD distribution. The extracted values of f_{exp} , plotted in Figure 3b as a function of hBN thickness (black line), reveal a quenching effect when the QDs are in direct proximity to the Au film. As the hBN spacer thickness increases, the PL intensity gradually rises, reaching a peak enhancement factor of approximately 7 at an hBN thickness of ~26 nm. Beyond this point, f_{exp} decreases with further increases in hBN thickness, eventually dropping below 1 when the thickness exceeds 100 nm.

This trend aligns with previous reports, which suggest that emitters with inherently low quantum yields (e.g., monolayer MoS₂ with $\eta = 10^{-3} - 10^{-4}$) experience minimal quenching when placed near a metal film, reducing the necessity for a dielectric spacer.³⁴ However, for

materials with relatively high quantum yields, such as the CsPbBr₃ QDs used in this study (intrinsic PLQY of 45.1% under 365 nm, 0.12 mW/cm² excitation), the nonradiative decay rate is a crucial factor, necessitating careful optimization of the emitter-metal spacing.^{23,34–36,56} The observed nonlinear dependence of PL enhancement on hBN thickness can be attributed to a combination of plasmon-induced enhancement of the incident electromagnetic field, an increased spontaneous emission rate due to the Purcell effect, and competing nonradiative processes, which will be discussed in detail later.

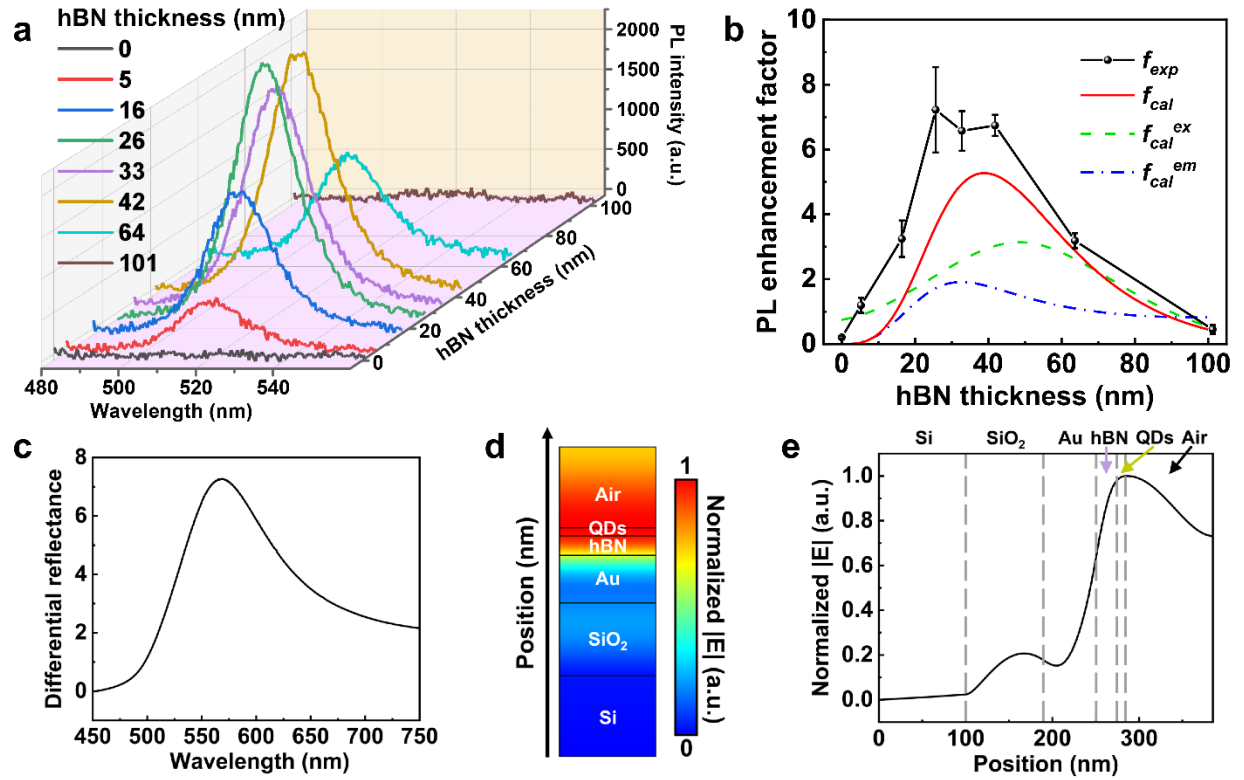


Figure 3. PL enhancement and simulation results for the mixed-dimensional heterostructure. (a) PL spectra of CsPbBr₃ QDs on hBN/Au heterostructures with hBN thicknesses ranging from 5 to 100 nm under continuous 405 nm excitation at an intensity of 10 W/cm². (b) PL enhancement factor as a function of hBN thickness: experimental data (black, f_{exp}), total simulated enhancement (red, f_{cal}), simulated excitation component (green, f_{cal}^{ex}), and simulated emission component

(blue, f_{cal}^{em}). Error bars represent statistical variation derived from scanning PL measurements. (c) Differential reflection spectrum of the Au nanoparticle film. (d) Simulated cross-sectional view of the local electric field amplitude $|\mathbf{E}|$ distribution across the heterostructure at an excitation wavelength of 405 nm and an hBN thickness of 26 nm. (e) Line profile of the electric field $|\mathbf{E}|$ at different positions in the heterostructure along the black arrow marked in (d).

To verify the role of surface plasmons in modulating the PL properties of the heterostructure, we conducted differential reflectance microscopy ($\Delta R/R$) measurements of the 60 nm Au nanoparticle film deposited on a SiO₂/Si substrate (Figure 3c). The results indicate a broad plasmonic resonance absorption peak centered at 568 nm, which overlaps significantly with the PL emission of CsPbBr₃ QDs (Figure 3a). This spectral overlap suggests an efficient interaction between excitons in the QDs and surface plasmons in the Au film, facilitating the observed PL enhancement. To analyze the PL enhancement, we model CsPbBr₃ QDs as randomly oriented electric dipoles under the statistical assumption, and decompose the surface plasmon contributions into two components: excitation rate enhancement at the incident wavelength and quantum yield enhancement at the emission wavelength. Accordingly, the PL enhancement factor f_{cal} is expressed as:

$$f_{cal} = \frac{\gamma_{ex}'}{\gamma_{ex}} \cdot \frac{\gamma_{em}'}{\gamma_{em}} = f_{cal}^{ex} \cdot f_{cal}^{em} \quad (1)$$

where γ_{ex} and γ_{em} represent the excitation rate at the incident wavelength and the spontaneous emission rate at the emission wavelength, respectively. The primed terms denote these values in the presence of the Au film.

Surface plasmons concentrate incident light into a localized region near the Au film, thereby enhancing the local electromagnetic field. This leads to an increase in the absorption cross-section

and subsequently raises the excitation rate γ_{ex}' for the excitonic system of CsPbBr₃ QDs. Since the exciton orientation of CsPbBr₃ QDs dispersed on the substrate is isotropically distributed, the excitation rate enhancement is proportional to the squared local electric field magnitude, $|\mathbf{E}|^2$. To examine this effect, we performed a numerical simulation for the local electric field distribution at an excitation wavelength of 405 nm and an hBN thickness of 26 nm (Figure 3d), based on the finite element method (FEM) (see Supporting Information for details). The simulation was conducted when f_{exp} reaches its maximum value. The simulation results reveal a substantial enhancement of the localized electromagnetic field at the QD position, leading to increased absorption of incident light. Figure 3e illustrates the spatial distribution of $|\mathbf{E}|$ at different positions in the heterostructure along the black arrow marked in Figure 3d.

Specifically, for plasmon-induced localized field enhancement in our heterostructure, the mechanism can essentially be interpreted as an optical interference process primarily involving the conductive Au layer, intrinsic hBN spacer, and semiconductor QD layer. The adjustment of hBN thickness effectively modulates the interference conditions to maximize the incident electric field intensity at the QD layer. For comparative analysis, Figure S7 displays the simulated local electric field amplitude $|\mathbf{E}|$ distribution across the optimized heterostructure (with 26 nm thick hBN) alongside those on a bare SiO₂/Si substrate. The functionality of the mixed-dimensional heterostructure is clearly demonstrated in this figure, where incident light excites surface plasmons that subsequently become concentrated near the QD layer. This concentration induces significant electromagnetic field amplification in the target region, thereby enhancing QD absorption. In stark contrast, this plasmon-induced enhancement effect is nearly absent in the bare SiO₂/Si substrate configuration. For reference, we also compared the PL spectra of CsPbBr₃ QDs spin-coated on different substrates including hBN/Au heterostructures, hBN/SiO₂/Si, SiO₂/Si, and quartz, as

shown in Figure S8. Additionally, the confocal PL scanning images of QDs on hBN/SiO₂/Si, SiO₂/Si, and quartz substrates are presented in Figure S9. The measurements in Figure S8 reveal distinct PL intensity variations among different insulating substrates, which can be attributed to substrate-dependent optical interference effects. For QDs on the hBN/Au heterostructure, they not only experience local field enhancement through the optical interference process involving the conductive Au layer, but also exhibit enhanced spontaneous emission rates via the Purcell effect, which is absent in other insulating substrates. Thus, the PL intensity of QDs on the hBN/Au heterostructure is significantly higher than that on other substrates.

Furthermore, to quantitatively determine the excitation component of the PL enhancement factor, we implemented a parametric scanning approach in the FEM simulation. This methodology simulated the electric field amplitude (denoted as $|\mathbf{E}'|$) at the QD layer position across varying hBN thicknesses from 0 to 100 nm. These values were compared against the reference electric field amplitude (denoted as $|\mathbf{E}|$) at the QD layer position in the SiO₂/Si substrate system. The excitation enhancement factor was then calculated as $f_{cal}^{ex} = \frac{\gamma_{ex}'}{\gamma_{ex}} = \frac{|\mathbf{E}'|^2}{|\mathbf{E}|^2}$, with the computational results plotted as the green line in Figure 3b.

In terms of quantum yield enhancement, the radiative transition rate γ is governed by Fermi's golden rule: $\gamma = \frac{2\pi}{\hbar^2} |\langle f | \hat{p} \cdot \hat{\mathbf{E}}_{vac} | i \rangle|^2 \rho(\omega)$. Here, γ represents the transition decay rate from the excited state $|i\rangle$ to the final state $|f\rangle$, $\hat{p}$ and $\hat{\mathbf{E}}_{vac}$ are the electric dipole and vacuum-field operators at the emitter's position, and $\rho(\omega)$ denotes the local photonic density of states.³² Given the highly confined nature of the plasmonic field, the local photonic density of states is significantly enhanced, leading to an increase in the spontaneous emission rate. To quantitatively analyze the Purcell effect in this system, we employed a semiclassical method previously reported in the literature.^{31,56} In our model, QD emitters are treated as an ensemble of randomly oriented oscillating dipoles

positioned at the top of the hBN layer. Using the dyadic Green's function approach for a dipole above a layered interface, we calculated the enhancement in the spontaneous emission rate due to the Purcell effect. Further details on these calculations can be found in the Simulation Section of the Supporting Information. The emission component of the PL enhancement factor, calculated as $f_{cal}^{em} = \frac{\gamma_{em}'}{\gamma_{em}}$, is plotted in Figure 3b as the blue line.

The red line in Figure 3b represents the total calculated PL enhancement factor, $f_{cal} = f_{cal}^{ex} \cdot f_{cal}^{em}$, demonstrating excellent agreement with the experimental data. This confirms that the observed enhancement results from the combined contributions of the localized electromagnetic field enhancement at the excitation wavelength and the Purcell effect at the emission wavelength. It is important to note that, in our simulations, the Au nanoparticle film was approximated as a planar metallic film for both excitation and emission enhancement calculations. This assumption neglects potential contributions from interparticle hotspots, where localized plasmonic effects could further enhance the incident field.^{32,34} The slight deviations between experimental data and simulation results in Figure 3b may stem from this simplification.

PL Decay Dynamics and Mechanistic Insights

We employed Jablonski diagrams (Figure 4a and 4b) to elucidate the Metal-enhanced PL mechanism.^{4,20} In the case of perovskite QDs in free space under optical excitation (Figure 4a), the excitonic system transitions from the ground state (S_0) to higher excited states (S_1 , S_2 etc.) upon absorbing incident light, with an excitation rate denoted as γ_{ex} . After undergoing internal conversion, which leads to relaxation to lower vibrational states, the system transitions back to the ground state, resulting in either radiative decay (Γ^{QDs}) via spontaneous emission or nonradiative decay rate (k_{nr}^{QDs}). When the perovskite QDs are placed near the Au nanoparticle film (Figure 4b), both excitation and emission rates are significantly altered due to strong exciton-plasmon

coupling. Upon illumination, surface plasmons are excited at the metal-dielectric interface, enhancing the local electromagnetic field and thereby increasing the excitation rate γ_{ex}^{pl} . Additionally, new decay channels emerge as excitons couple to surface plasmons, leading to an enhanced decay rate (Γ_c^{QDs}) due to energy transfer into surface plasmon modes. Concurrently, nonradiative quenching (k_q^{QDs}) becomes relevant, which is induced by the presence of metal through nonradiative energy dissipation. The energy transferred to surface plasmons modes can either be radiatively emitted (Γ^{pl}) or lost through nonradiative decay (k_{nr}^{pl}). The quantum yield (η_0) and PL lifetime (τ_0) of perovskite QDs in free space can be expressed as:

$$\eta_0 = \Gamma^{QDs} \tau_0 \quad (2)$$

$$\tau_0 = \frac{1}{\Gamma^{QDs} + k_{nr}^{QDs}} \quad (3)$$

However, in the presence of the plasmonic system, both parameters are modified due to the Purcell effect, and the modified quantum yield (η) and PL lifetime (τ) are given by:

$$\eta = (\Gamma^{QDs} + \Gamma^{pl}) \tau \quad (4)$$

$$\tau = \frac{1}{\Gamma^{QDs} + \Gamma^{pl} + k_{nr}^{QDs} + k_q^{QDs} + k_{nr}^{pl}} \quad (5)$$

By carefully tuning the thickness of the hBN dielectric spacer, we can optimize the radiative decay rate ($\Gamma^{QDs} + \Gamma^{pl}$) while minimizing nonradiative losses ($k_{nr}^{QDs} + k_q^{QDs} + k_{nr}^{pl}$). This adjustment helps reduce quenching effects while maintaining efficient exciton-plasmon coupling. Specifically, hBN serves to hinder direct charge transfer from CsPbBr₃ quantum dots to the Au nanoparticle film and suppresses nonradiative relaxation processes. In this regard, its function parallels that of conventional dielectric spacers such as SiO₂,^{4,56} Al₂O₃,^{57–59} or polymers (e.g., PE or PMMA),^{23,60} which have been extensively utilized in previous studies of plasmonic systems.

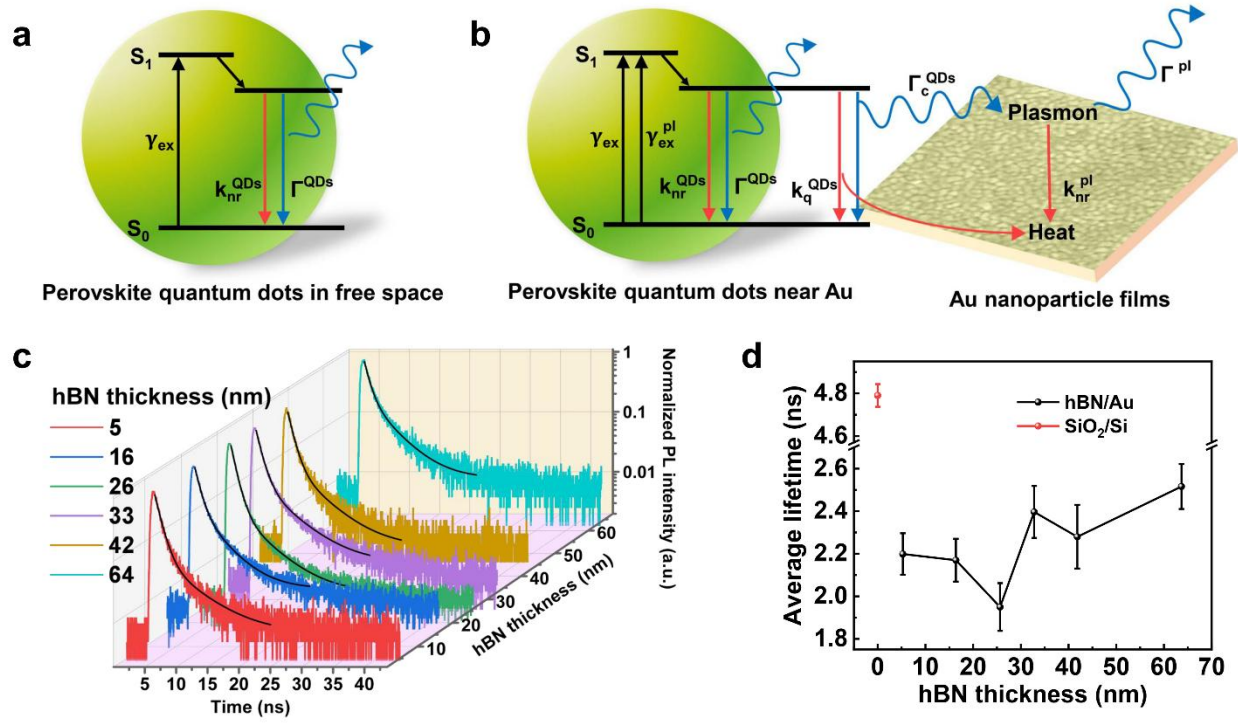


Figure 4. Energy diagrams and PL decay dynamics. Jablonski diagrams illustrating the energy transfer pathways when perovskite quantum dots are (a) in free space and (b) near Au nanoparticle films. S_1 : Excited state, S_0 : Ground state, γ_{ex} : Excitation rate by absorption of incident light, k_{nr}^{QDs} : Intrinsic nonradiative decay rate of QDs, Γ^{QDs} : Intrinsic radiative decay rate of QDs, γ_{ex}^{pl} : Metal-enhanced excitation rate, k_q^{QDs} : Nonradiative quenching of QDs by Au, Γ_c^{QDs} : Enhanced decay rate of QDs by energy conversion into surface plasmon mode, Γ^{pl} : Radiative decay rate of plasmon, k_{nr}^{pl} : Nonradiative decay rate of plasmon. (c) TRPL curves of CsPbBr₃ QDs on hBN/Au heterostructures with varying hBN thicknesses under pulsed 375 nm excitation at an intensity of 10 W/cm², fitted with biexponential decays (solid black lines). (d) Average PL lifetime as a function of hBN thickness, compared to SiO₂/Si substrate. The error bars reflect fitting uncertainty.

To experimentally examine the influence of surface plasmons on the decay dynamics of CsPbBr₃ QDs, we employed FLIM to measure the PL lifetime of QDs on both the hBN/Au

heterostructure and bare SiO₂/Si substrates (Figure 2d). The time-resolved PL (TRPL) curves extracted from FLIM measurements, shown in Figure 4c, provide a quantitative assessment of the PL lifetime as a function of hBN thickness. For heterostructures with 0 nm and 101 nm hBN thickness, the TRPL curves are not displayed due to insufficient photon counts, likely caused by severe plasmon-induced quenching. A direct comparison of TRPL results for CsPbBr₃ QDs on the optimized heterostructure (26 nm hBN/Au) and on the bare SiO₂/Si substrate is provided in Figure S10 in the Supporting Information. The PL lifetime of QDs on the heterostructure (τ) is significantly shorter than that on the SiO₂/Si substrate (τ_0), confirming that the presence of the Au film modifies the emission dynamics, as predicted by the PL lifetime modification equations.

All the TRPL curves in Figure 4c were well fitted using a bi-exponential function, $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. From these fits, the average PL lifetime ($\bar{\tau}$) was calculated as $\bar{\tau} = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$ of QDs. The results, plotted in Figure 4d, demonstrate that the average lifetime of CsPbBr₃ QDs on the bare SiO₂/Si substrate is $\bar{\tau}_0 = 4.79$ ns. For QDs on the heterostructure, the average lifetimes vary with hBN thickness, yielding values of 2.20, 2.17, 1.95, 2.40, 2.28, and 2.52 ns for hBN thicknesses of 5, 16, 26, 33, 42, and 64 nm, respectively. The corresponding fitting parameters, including decay constants (τ_1 , τ_2), amplitude ratios (A_1 , A_2), and calculated average lifetimes ($\bar{\tau}$), are tabulated in Table S3 in the Supporting Information.

The observed trend directly correlates with the PL enhancement behavior as a function of hBN thickness: the PL lifetime initially decreases, reaching a minimum at ~26 nm hBN, which coincides with the maximum PL enhancement factor of 7-fold. Beyond this optimal thickness, the PL lifetime gradually increases, mirroring the decline in PL enhancement. This correlation suggests that stronger PL enhancement is generally associated with shorter PL lifetimes, confirming that an appropriate hBN thickness optimizes exciton-plasmon interactions. At ~26 nm

hBN, the increase in radiative decay rate (Γ^{pl}) is sufficient to counteract the concurrent increase in nonradiative decay channels ($k_{\text{q}}^{\text{QDs}} + k_{\text{nr}}^{\text{pl}}$) caused by exciton-plasmon coupling. In addition, the CsPbBr₃ QDs always exhibit shorter PL lifetimes when directly placed on Au films (0 nm hBN thickness) or Au-hBN heterostructures compared to the bare SiO₂/Si control substrate. This reduction can be attributed to the introduction of additional radiative (Γ^{pl}) and nonradiative decay channels ($k_{\text{q}}^{\text{QDs}} + k_{\text{nr}}^{\text{pl}}$) arising from the Au nanoparticle film, which collectively accelerate the depopulation of excited states and consequently diminish the PL lifetime ($\bar{\tau}$) of the quantum dots. For reference, we also compared the time-resolved PL spectra of CsPbBr₃ QDs spin-coated on different substrates including hBN/Au heterostructures, hBN/SiO₂/Si, SiO₂/Si, and quartz, as shown in Figure S11. The measurement results demonstrate that the QD lifetimes on insulating substrates (hBN/SiO₂/Si, SiO₂/Si, and quartz) show no significant differences, while the lifetime on hBN/Au heterostructures is substantially lower than those on all insulating substrates, which aligns with our aforementioned discussion results.

To comparatively investigate whether the excitation fluence of incident light affects the PL enhancement factor, we also conducted parallel measurements of PL and TRPL for CsPbBr₃ QDs on hBN/Au and SiO₂/Si substrates under varying incident light fluences. Figure S12 presents the PL intensity and average lifetime of QDs as functions of laser power density under continuous 405 nm excitation and pulsed 375 nm excitation, respectively. Experimental results demonstrated that within the laser power density range of 4-15 W/cm², both the PL enhancement factor and average lifetime of QDs on both substrates exhibited no discernible regular trends, suggesting that no significant changes in exciton dynamics occurred within this power density range. This observation validates the reliability of employing 10 W/cm² excitation power density for analyzing PL enhancement and lifetime characteristics throughout our experimental investigations.

CONCLUSIONS

In summary, we demonstrated a 0D-2D-3D mixed-dimensional van der Waals heterostructure that significantly enhances the photoluminescence of CsPbBr₃ perovskite quantum dots through plasmon-induced field amplification and the Purcell effect. By optimizing the hBN dielectric spacer thickness (~26 nm), we achieved a seven-fold enhancement in PL intensity while reducing the PL lifetime, confirming increased radiative decay. Theoretical modeling and numerical simulations validated the experimental findings, attributing the enhancement to localized electromagnetic field enhancement and modified spontaneous emission rates. In future applications, the plasmonic system enhances the internal quantum efficiency of perovskite QDs, thereby enabling direct improvement in the performance of perovskite quantum dot light-emitting diodes. Concurrently, incident photons excite plasmon modes that concentrate electromagnetic fields near the perovskite QD layer, thereby boosting light absorption in QDs—a critical advantage for enhancing the efficiency of photodetectors and phototransistors. Our work provides valuable insights into exciton-plasmon coupling mechanisms in hybrid perovskite-plasmonic systems, establishing a design framework for high-efficiency quantum photonic devices through metal-enhanced photoluminescence.

EXPERIMENTAL SECTION

Materials. All chemical reagents, including hexane (anhydrous HEX, Sigma-Aldrich, 98%), ethyl acetate (EA, Sigma-Aldrich, 90%), PbBr₂ (Sigma-Aldrich, 99.99%), Cs₂CO₃ (Sigma-Aldrich, 99.99%), octadecene (Sigma-Aldrich, ODE, 90%), oleylamine (OAm, Aladdin, 90%), and oleic acid (OA, Sigma-Aldrich, 90%), were used as purchased without further purification.

Fabrication of colloidal CsPbBr₃ quantum dots (QDs). For the preparation of the Cs-OA precursor, a 25-mL three-necked flask was charged with Cs₂CO₃ (0.407 g), OA (1.25 mL), and

ODE (20 mL). The mixture was then degassed under vacuum at 120 °C for 1 hour and heated to 150 °C under an Ar atmosphere until the reaction between the OA and Cs₂CO₃ was completed.

For the synthesis of CsPbBr₃ QDs, PbBr₂ (0.138 g) and ODE (10 mL) were introduced into a 25-mL three-necked flask. The mixture was heated at 120°C for 1 hour under vacuum, followed by the introduction of argon into the flask. Subsequently, pre-dried OAm (1 mL) and OA (1 mL) were added to the mixture. The reaction flask was then heated to 160°C until the solution turned clear. Preheated cesium oleate (0.8 mL) was rapidly injected into the flask. After a reaction time of 5 seconds, the flask was cooled to room temperature using ice water.

For the isolation and purification, the crude solution of CsPbBr₃ QDs was poured into a centrifuge tube and centrifuged at 10,000 rpm for 10 minutes. The precipitate was redispersed in 4 mL of n-hexane, mixed with 8 mL of ethyl acetate, and then centrifuged again at 10,000 rpm for 5 minutes. The final precipitate was distributed in 2 mL of n-hexane.

Fabrication of CsPbBr₃ QDs, hBN and gold film mixed-dimensional van der Waals (vdW) heterostructure. The 60 nm gold film was deposited by thermal evaporation onto the top of a 90 nm SiO₂/Si substrate under nitrogen atmosphere. Multilayer hBN flakes were first mechanically exfoliated onto PDMS (Gel-pak, PF-40/17-X4) from a high-quality hBN bulk crystal using Scotch tape, and then transferred onto the Au film. The CsPbBr₃ quantum dot film was fabricated by spin-coating 40 µl of the diluted QD colloidal solution onto the top of the as-fabricated hBN-Au-SiO₂/Si structure at 3000 rpm for 60 seconds.

Characterizations. The TEM images were obtained at an accelerating voltage of 200 kV using a JEOL JEM-2100F transmission electron microscope. For TEM sample preparation, the CsPbBr₃ quantum dots were first dispersed in n-hexane solution and subjected to ultrasonication at 60 Hz. Subsequently, several drops of the well-dispersed suspension were drop-cast onto a

copper grid and allowed to air-dry completely prior to imaging. To minimize potential electron beam-induced damage to the quantum dot crystal structure, the imaging duration for each selected region was limited to under 10 minutes throughout all imaging sessions.

The UV-vis absorption measurements were conducted under ambient conditions using a tungsten halogen lamp (HL10000-Mini, Oceanhood) as the excitation light source. The sample (quantum dot colloidal solution, approximately 3 mL) was placed in a standard $12.5 \times 12.5 \times 45$ mm quartz cuvette with a 10 mm optical path length. The transmitted light was coupled into a fiber optic spectrometer (XS11639, Oceanhood) through an SMA905 optical fiber to obtain the absorption spectrum.

The AFM measurements were conducted under ambient conditions using a Bruker Innova instrument. The surface topography measurements were operated in tapping mode with metallic AFM probes (MikroMasch, HQ:NSC15/Cr-Au).

The confocal PL mapping was carried out under ambient conditions using a scanning confocal fluorescence microscope (Horiba, XploRA PLUS). A 405 nm solid-state laser was used as the excitation source and focused on the samples through a $20\times$ objective lens (N.A. = 0.40). The system was equipped with a 150 grooves/mm holographic grating and a confocal attachment, and the PL emission was detected using a Peltier-cooled electron multiplying CCD (SIN-EM FIVIS).

The FLIM measurements were performed under ambient conditions using a PicoQuant MicroTime200 system integrated with an Olympus microscope. A 375 nm pulsed laser, operating at a 20 MHz repetition rate, was used as the excitation source. The incident laser intensity was controlled using a variable neutral density filter (Lbtek, NDFR-50S-3M), and then passed through a 500 nm shortpass filter (Jcoptix, OFE1SP-500) and a 375 nm dichroic beam splitter, and finally focused onto the sample surface using an objective lens (Olympus MPLFLN20 $\times$, N.A. = 0.40).

The emitted PL signal from the sample was collected by the same objective, passed through the dichroic beam splitter and a 405 nm long pass filter, followed by a second variable neutral density filter, a 300 nm confocal pinhole, and finally detected by a single-photon avalanche diode (SPAD). The electrical signals were processed using time-correlated single-photon counting (TCSPC) electronics (PicoQuant, TimeHarp 260). In the presented FLIM images, the PL intensity and PL lifetime are both derived from the signals collected by the single-photon detector at the same excitation spot. Specifically, the PL intensity reveals the counts of photons collected, which affects the brightness of the image, labeled as a gray scale, and the PL lifetime reveals the intensity weighted average lifetime, which affects the pseudocolor of the image, labeled as a rainbow scale.

The differential reflectance spectra ($\Delta R/R$) were acquired under ambient conditions using a spectrometer system (EasySpec, Metatest corporation) equipped with a halogen lamp. To obtain the $\Delta R/R$ spectra, we measured the reflectance spectra of the sample (Au nanoparticle film), denoted as I_{sample} , and the corresponding bare SiO₂/Si substrate (uncoated region), denoted as $I_{substrate}$. The differential reflectance spectra were then defined as $\Delta R/R = (I_{sample} - I_{substrate})/I_{substrate}$.

The PLQY measurements were carried out under ambient conditions using Edinburgh Instruments Spectrofluorometer FS5. The excitation source employed was a xenon lamp operating at 365 nm wavelength with an irradiation intensity of 0.12 mW/cm².

The measurement of incident light power density was performed using a power meter (Thorlabs, PM100D) equipped with a microscope slide power meter photodiode sensor head (Thorlabs, S170C). The incident power was first measured in a dark environment, and subsequently the light spot diameter was determined through microscopic measurements, enabling the calculation of the power density.

ASSOCIATED CONTENT

Data Availability Statement

Data underlying the results presented in this paper are not publicly available at this time but maybe obtained from the authors upon reasonable request.

Supporting Information

The Supporting Information is available free of charge.

Detailed description of experimental and simulation section; supplementary results of PLQY, PL, TRPL

AUTHOR INFORMATION

Corresponding Authors

Minliang Lai – School of Nano Science and Technology, Suzhou Institute for Advanced Research, University of Science and Technology of China, Suzhou, Jiangsu 215123, China; Email: mllai@ustc.edu.cn

Jia Lin – Department of Physics, Shanghai University of Electric Power, Shanghai 200090, China; Email: jlin@shiep.edu.cn

Sheng Wang – Key Laboratory of Artificial Micro-and Nano-structures of Ministry of Education, and School of Physics and Technology, Wuhan University, Wuhan, Hubei 430072, China; Wuhan Institute of Quantum Technology, Wuhan, Hubei 430206, China; orcid.org/0000-0001-7923-478X; Email: shengwang16@whu.edu.cn

Author Contributions

[§]K.Z., J.Z. and R.M. contributed equally to this work. S.W. conceived, designed, and supervised the research. K.Z. fabricated the mixed-dimensional heterostructure, conducted the PL, absorption and differential reflection measurements as well as performed the simulation. W.Z. and Z.X. conducted the AFM measurement. J.Z. and S.C. conducted the FLIM measurements. R.M., Y.Zhou and M.Li. prepared the colloidal solution of CsPbBr₃ QDs and conducted the TEM measurements under the supervision of Y.W. and J.L.. Y.Zhao conducted the PLQY measurements under the supervision of M.Lai. K.W. and T.T. provided the h-BN crystals. K.Z. and S.W. analyzed the data and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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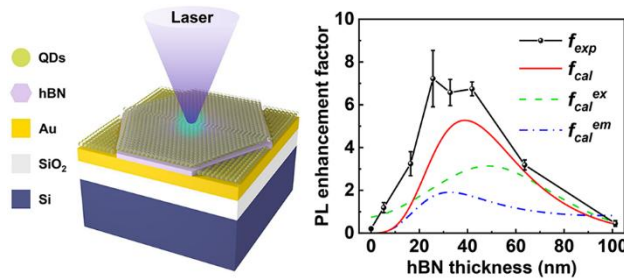
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Metal-enhanced Photoluminescence in Perovskite Quantum Dots-hBN-Gold Film Mixed-dimensional Van der Waals Heterostructure

*Kunjie Zhou^{1§}, Jingyi Zhu^{1§}, Ruisi Meng^{2§}, Wei Zeng¹, Zhuo Xue¹, Chen Shen¹, Yueran Zhao³,
Yuchen Zhou², Mengyao Li², Yanan Wang², Kenji Watanabe⁴, Takashi Taniguchi⁵, Minliang
Lai^{3*}, Jia Lin^{2*}, and Sheng Wang^{1,6*}*

TOC GRAPHICS



Brief synopsis: A pioneering 0D-2D-3D mixed-dimensional van der Waals heterostructure is introduced, composed of 0D semiconducting CsPbBr₃ quantum dots, 2D insulating multilayer hexagonal boron nitride (hBN), and 3D conducting gold nanoparticle film. A maximum PL enhancement of 7-fold at an hBN thickness of 26 nm is achieved, and the theoretical simulations further corroborate the experimental observations.