

Confinement-dependent exciton and biexciton dynamics in bright band-gap-emitting AgInS₂ quantum dots

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(Received 16 June 2026; revised 3 August 2026; accepted 4 August 2026; published 26 August 2026)

I-III-VI quantum dots are potential candidates for light-emitting and light-harvesting applications due to their heavy-metal-free composition and chemical tunability. Despite their potential, the investigation of intrinsic exciton and excitonic many-body dynamics has often been complicated because of their extensive defect energy landscape. Here, we investigate bright band-gap-emitting AgInS₂ quantum dots of sizes ranging from ~ 4 to 7 nm using femtosecond pump-probe spectroscopy to link quantum confinement to exciton formation and many-body interactions. The exciton formation time is governed by inter-valence-band hole relaxation. This increases by more than a factor of 4 with decreasing quantum dot size, reflecting size-dependent exciton-phonon scattering efficiency. By temporally correlating hole relaxation with induced absorption dynamics, we identify different exciton-to-biexciton transitions originating from different exciton states. Excitation-fluence-dependent measurements reveal a biexciton decay time that scales with the quantum dot volume. Smaller quantum dots show fast decay of < 100 ps, primarily governed by exciton-exciton annihilation. In larger quantum dots, the biexciton lifetime exceeds 400 ps, indicating reduced annihilation efficiency. Complementary streak-camera photoluminescence experiments provide direct spectroscopic evidence that these long-lived biexcitons are partially emissive. Collectively, we report an in-depth ultrafast-optical study yielding fundamental insights into the complex landscape of exciton formation and biexciton physics, which advances the understanding of intrinsic optical processes in AgInS₂ quantum dots among I-III-VI materials.

DOI: [10.1103/9nj2-4hb1](https://doi.org/10.1103/9nj2-4hb1)

I. INTRODUCTION

Environmentally friendly, narrow-emitting I-III-VI quantum dots (QDs), in particular colloidal AgInS₂ QDs, are gaining popularity as a promising alternative to the well-established heavy-metal-containing Pb- and Cd-based QDs [1–8]. They excel due to their low toxicity, remarkable stability, flexible chemical composition, and broadly tunable optical properties. In contrast, both Pb and Cd are listed as restricted substances under the European Union's RoHS directive, constraining their use in commercial devices. This makes I-III-VI QDs especially interesting for optoelectronic applications, such as light-emitting devices (LEDs), wide color gamut display technologies, biological imaging and sensing, as well as energy harvesting applications.

In general, QDs are zero-dimensional (0D) nanocrystals, where quantum confinement arises when their radius is comparable to the exciton Bohr radius. Depending on the size of the QD, confinement leads to discrete states through the quantization of the center-of-mass motion of weakly confined Wannier-Mott excitons or the separate quantization of individual electrons and holes in the strong confinement limit [9]. The discretization of electronic states gives rise to the phonon bottleneck, where carrier-phonon scattering is inefficient not only because the available phonon energies mismatch the spacing between quantized levels, but also due to a strongly suppressed spatial overlap between excitons (or electron/hole) and phonon wave functions [10,11]. In strongly confined systems, however, the Coulomb exchange interaction between electrons and holes enables efficient energy transfer between them [12–14]. This results in rapid carrier relaxation, thereby bypassing the phonon bottleneck.

Importantly, pronounced excitonic effects in QDs result in biexciton formation through many-body interactions [15–19]. Biexcitons originate from the Coulomb interaction between two excitons, leading to the formation of a bound two-exciton state. The interaction strength is thereby characterized by the biexciton binding energy, which is reported in the range of tens to hundreds meV for Cd- and Pb-based QDs, depending on their size [19–25]. Pioneering work by Klimov *et al.*,

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among others, provided fundamental insights into such excitonic many-body interactions [26]. This includes, e.g., the size dependence of three-body Auger recombination, two-body exciton-exciton annihilation (EEA), and biexciton transitions. For instance, biexciton emission is enhanced in CdSe QDs with a giant shell exhibiting biexciton decay times in the ns regime [27]. Consequently, nonradiative many-body interactions are suppressed. In contrast, biexciton lifetimes in Pb-halide perovskite QDs are below 100 ps [23,25,28,29]. These fast biexciton decay times originate from efficient nonradiative excitonic many-body interactions. Such an understanding of biexcitons, EEA, and Auger recombination processes in QDs is crucial for designing efficient LEDs and lasing materials.

In I-III-VI QDs, intrinsic excitonic many-body interactions remain largely unexplored compared to well-established QD systems, where, e.g., scaling relationships have served as foundational references for the field [26]. This is mainly because point defects can trap charge carriers on subpicosecond timescales [30]. For example, Debnath *et al.* reported probe-induced biexcitons associated with a pump-generated high-energy exciton and a probe-induced exciton trapped at an antisite-defect state in broad-emitting Cu-In-S- and Ag-In-S-based QDs [31,32]. Furthermore, trap-assisted Auger recombination in defect-emitting CuInS₂ QDs was examined, involving a free electron and a trapped hole at a Cu vacancy [33]. For CuInS₂ QDs with sizes ranging from 2.8 to 3.4 nm, all showing broad emission, Auger recombination was observed on the timescale of 10–23 ps [34]. Similarly, an optical study on broad-emitting CuInSe₂ QDs showed size-dependent Auger recombination times of 73, 85, and 130 ps for QDs of 4.5, 6.2, and 9.2 nm, respectively [35]. Recent advances in defect control in Ag-In-S-based QDs have shown that careful surface engineering can suppress such trap states and enable free-exciton emission with narrow photoluminescence (PL) [4,5]. As reported by our group, defect management not only improves optical quality but also reveals the intrinsic excitonic nature of I-III-VI QDs [30]. This provides a platform to study their fundamental photophysics, which are determined by the electronic structure. Unlike the degenerate valence-band maximum (VBM) of traditional II-VI or III-V semiconductors, Ag-based I-III-VI compounds exhibit an isolated upper valence band that is split from the lower bands [30,36]. This splitting originates from their noncubic unit cells, where the anisotropic crystalline field lifts the valence-band degeneracy. As a result, excitons can be optically formed at these distinct band-edge states. The resulting excitonic many-body interactions arising from the split valence-band structure may create a complex landscape of transitions that remains poorly understood.

In this study, we investigate narrow free-exciton-emitting AgInS₂ QDs with PL quantum yields (PLQYs) of up to 56%. By tuning the QD size, the emission color is varied from green to red, allowing us to establish a sizing curve for AgInS₂ semiconductors and enabling the exploration of ultrafast-optical processes that depend on the degree of confinement. Ultrafast transient transmission spectroscopy reveals the dynamics of hole relaxation and exciton formation, showing a pronounced size dependence. Smaller QDs show delayed hole relaxation times due to reduced exciton-phonon

scattering efficiency. We further probe and identify exciton-exciton interactions through induced-absorption transitions from excitons to biexcitons arising from different valence-band states. Utilizing fluence-dependent pump-probe measurements, we determine lifetimes ranging from 70 to 495 ps from small to large QDs and establish a scaling law for biexciton decay in AgInS₂ QDs. The longer biexciton lifetime in larger QDs suggests emissive biexcitons. This is corroborated by excitation-fluence-dependent streak measurements, where a blue shift in the PL spectrum on the timescale of the biexciton decay is observed. These findings uncover the intrinsic exciton and biexciton dynamics in narrow free-exciton-emitting I-III-VI QDs, overcoming defect-trapping effects and establishing systematic scaling relationships that address a longstanding research gap, thereby advancing understanding beyond II-VI and III-V systems.

II. RESULTS AND DISCUSSION

We synthesize AgInS₂ QDs of five different sizes using a modified procedure reported by us previously (see the Methods section for details on synthesis) [30]. Representative scanning transmission electron microscopy in high-angle annular dark-field (STEM-HAADF) images in Fig. 1(a) show highly crystalline QDs with a lattice fringe distance of 0.35 nm, consistent with the AgInS₂ chalcopyrite structure. STEM-HAADF images on a larger scale are depicted in Fig. S1 in the Supplemental Material (SM) [37]. Using x-ray diffraction (XRD), we confirm that the QDs crystallize in the tetragonal AgInS₂ phase [Fig. 1(b) and Fig. S2 in the SM [37]]. The QD sizes are determined by small-angle x-ray scattering (SAXS, Fig. S3 in the SM [37]), yielding diameters in the range of 4.4–7 nm, which is in good agreement with the crystalline sizes determined from the Debye-Scherrer analysis of XRD data.

Figure 1(c) shows the absorption and PL spectra of the different-sized QDs. At shorter photon wavelengths, the absorbance increases continuously, indicating a quasicontinuum of closely spaced excitonic states that arise from quantization of the center-of-mass motion and different band states. Below the quasicontinuum, the absorption spectra display two exciton transitions, X1 and X2. Earlier, we presented that these excitonic transitions originate from electron states derived from the conduction-band minimum (CBM) and hole states derived from the two uppermost VBMs [30]. A schematic illustration of the band structure of AgInS₂ is shown in Fig. 1(d) (left). In the quantum-confined system, the k -space dispersion is lost [9]. Accordingly, these continua evolve into discrete levels associated with the corresponding excitons [Fig. 1(d), right]. Interestingly, the holes in the two uppermost valence bands exhibit comparable confinement behavior [30]. As a result, the energy separation between X1 and X2 in our QDs remains nearly constant (~ 160 meV) under quantum confinement (Fig. S4 in the SM [37]). This X1-X2 splitting is consistent with electroluminescence measurements on AgInS₂ bulk crystals [38]. Notably, the transition from a k -space dispersed to a discrete electronic system occurs smoothly and depends on the degree of quantum confinement. The PL spectra exhibit narrow emissions, attributed to free-exciton recombination, with PLQYs ranging from 31% to 56%. For

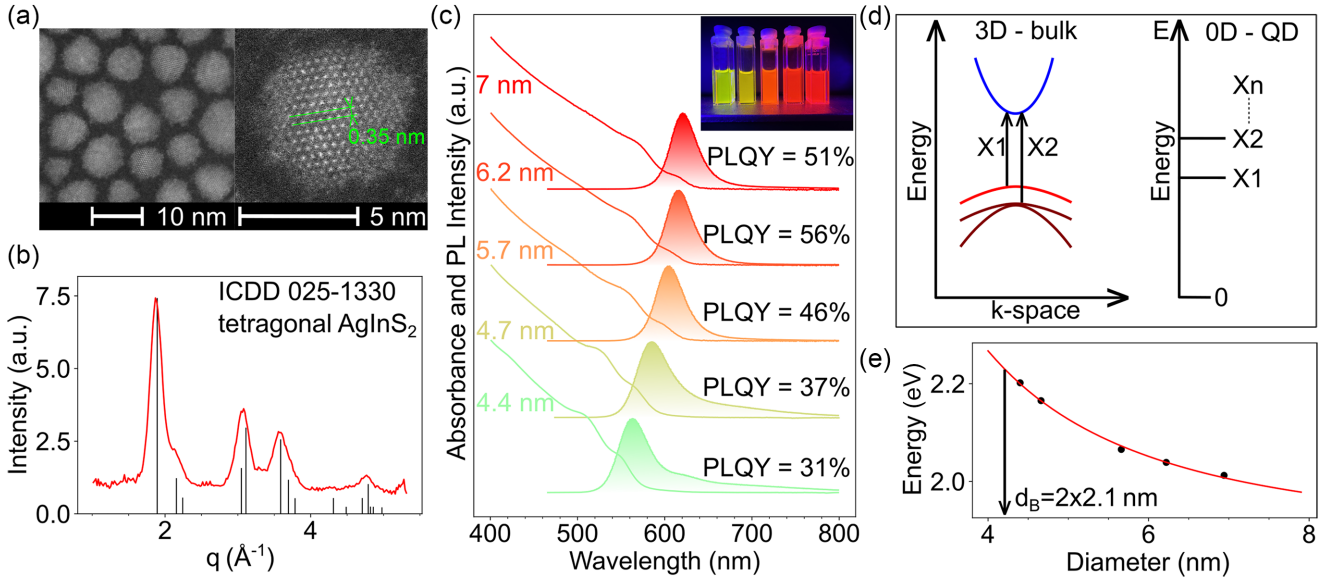


FIG. 1. (a) Representative STEM-HAADF images of 6.2 nm AgInS₂ QDs. (b) A representative XRD pattern of the smallest 4.4 nm AgInS₂ QDs. (c) Absorption and PL spectra of different-sized AgInS₂ QDs, ranging from 4.4 to 7 nm in diameter, with PLQY values up to 56%. The inset shows a cuvette image of the corresponding AgInS₂ QDs under UV-light illumination. (d) On the left side, a schematic representation of the band structure of AgInS₂ [30], consisting of three upper valence bands and a conduction band, is shown. The exciton transitions X1 and X2 are depicted, associated with two valence-band maxima. On the right side, the excitons are presented in the two-particle picture without dispersion for the quantum-confined system. (e) Energy dependence of the exciton X1 on the diameter of the AgInS₂ QDs, including the exciton Bohr radius.

QDs of size 4.4 and 4.7 nm, a weak, additional broad emission appears on the long-wavelength side, owing to the presence of point defects, likely due to the higher surface-to-volume ratio [39]. Figure 1(e) shows the QD size-dependent shift of the exciton state X1 in a sizing curve. Exciton X1 blueshifts with decreasing QD size, consistent with the quantum confinement effect. The data points are fitted using the confinement in a spherical potential model $E(d) = \hbar^2 \pi^2 / [2\mu(d/2)^2] + E_{\text{bulk}}$, with μ being the reduced effective mass and d being the diameter of the QDs and E_{bulk} denoting the bulk band gap [9]. From the fit, we obtain a bulk band gap of 1.88 eV in close agreement with the experimentally obtained 1.86 eV [38]. Further, we deduce the reduced effective mass $\mu = 0.24m_0$, with m_0 being the free-electron mass, in good agreement with values reported from DFT calculations [30,40,41]. From this parameter, we determine the exciton Bohr diameter, indicated by the arrow in Fig. 1(e). All QD sizes are larger than the exciton Bohr diameter, confirming that the system lies in the weak-confinement regime. Notably, for strongly confined nanocrystals, the confinement energy can scale with an exponent deviating from 2, which can further be influenced by shell-related transitions and defects [42–44]. However, for the free-exciton-emitting core-only QDs in the weak-confinement regime (being relevant here), the effective-mass description with a quadratic dependence is appropriate.

Femtosecond pump-probe spectroscopy is employed to investigate the transient changes in the intrinsic excitonic transitions of the different-sized AgInS₂ QDs. Figure 2(a) shows representative differential transmission (DT) spectra for 4.7 nm QDs at various delay times under low excitation fluence (average number of excitations: $\langle N \rangle \approx 0.1$ at 400 nm pump). Three distinct spectral features are observed, including two

positive signals and one negative signal, which are indicated by the colored shaded regions in Fig. 2(a). We observe equivalent spectral features for the other sizes (4.4, 5.7, 6.2, and 7 nm QDs shown in Figs. S8A, S9A, S10A, and S11A, respectively, in the SM Sec. II A [37]). The two positive DT features coincide spectrally with the excitonic transitions X1 and X2 in the corresponding linear absorption spectrum and are therefore attributed to bleaching signals due to state filling of X1 and X2 [45]. The negative feature on the long-wavelength side of the X1 bleach corresponds to an exciton-to-biexciton absorption, arising from exciton-exciton Coulomb interaction involving X1 [16,19]. In this process, the pump pulse creates a single exciton that interacts with a probe-generated exciton X1 to form a bound biexciton state (XX). The biexciton energy (E_{XX}) is reduced relative to the sum of two single-exciton energies ($2E_X$) by the biexciton binding energy ($E_{\text{XX}} = 2E_X - E_{\text{b,XX}}$), resulting in the redshifted induced-absorption feature.

In the following, we demonstrate that inter-valence-band hole relaxation is delayed with decreasing QD size, due to reduced exciton-phonon scattering efficiency in smaller QDs. The temporal evolution of the X1 and X2 bleach amplitudes for 4.7 nm QDs is shown in Fig. 2B. Evidently, transient X2 rises faster than X1, which is composed of two distinct rise components. First, a fast <200 fs process is attributed to the population of the band-edge electron state. Second, a slower component corresponds to inter-valence-band hole relaxation between the two lowest hole states ($X2 \rightarrow X1$). In this process, the DT signal at X2 does not decay significantly because the excited electron continues to occupy the conduction-band state. On the long-time scale, both X1 and X2 transients display identical decays (Fig. S5A in the SM [37]) governed by the depopulation of electrons, consistent with our previous

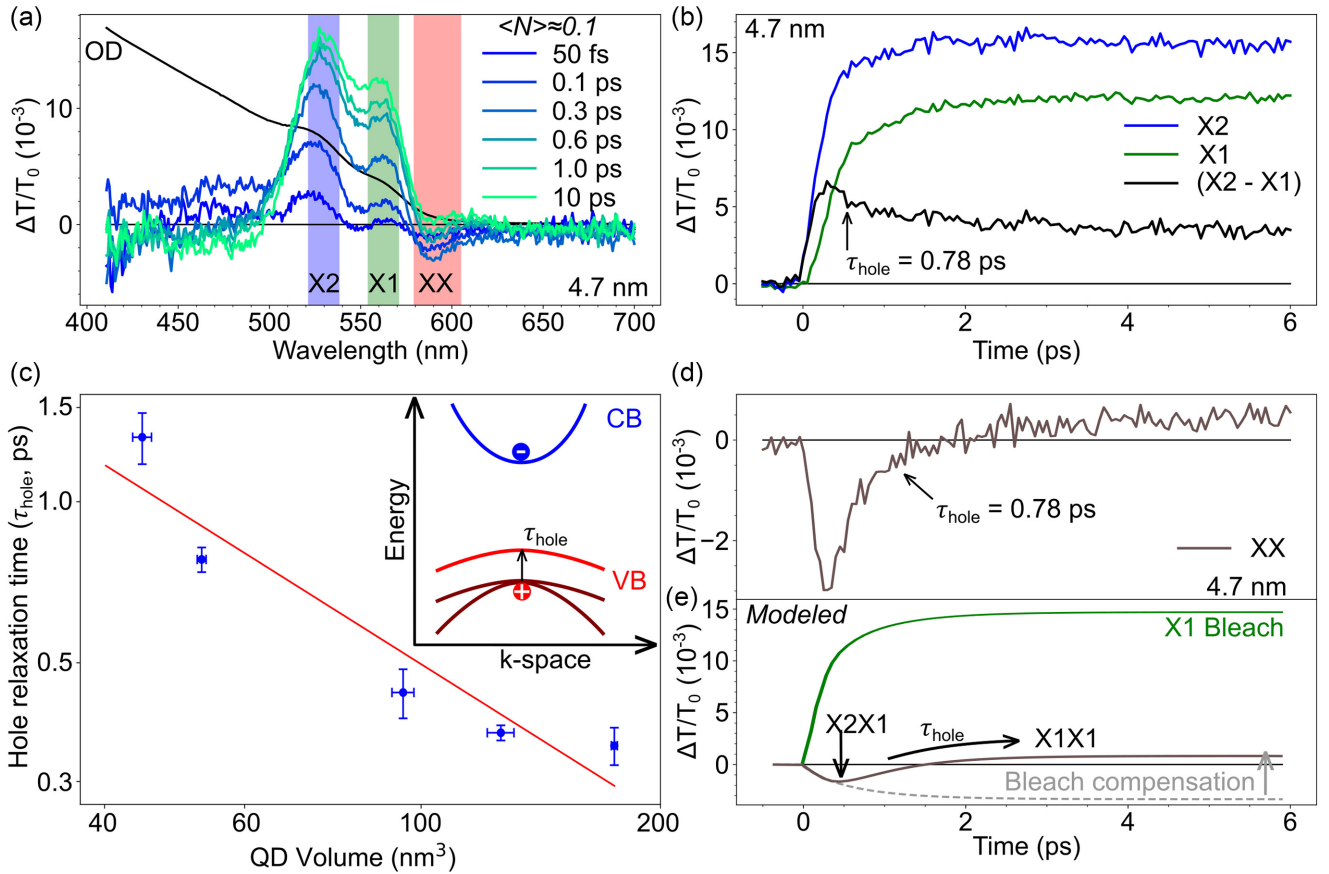


FIG. 2. (a) DT spectra at various delay times upon 400 nm excitation of 4.7 nm AgInS₂ QDs. In the shaded areas, state-filling of exciton X1 and X2, as well as the biexciton induced absorption, are shown. For reference, the steady-state absorption is shown in black. (b) Transients of bleach X2 (524 nm) and X1 (565 nm) in blue and green, respectively. In black, we present the difference between them, yielding the hole relaxation time τ_{hole} . The signals are not affected by chirp artifacts, as evidenced in Fig. S6 in the SM [37]. (c) Logarithmic scale plot of hole relaxation times and QD volume. The inset shows a scheme of the inter-valence-band hole relaxation. (d) The biexciton-induced absorption transients at 588 nm for 4.7 nm QDs. (e) Model transients for exciton X1 bleach in green, induced absorption in brown, and the induced absorption in dashed gray without bleach spectral overlap, compensating the negative signal.

report [30]. The hole relaxation time τ_{hole} is obtained by subtracting the X1 from the X2 bleach transient, yielding $\tau_{\text{hole}} = (0.78 \pm 0.04)$ ps for 4.7 nm QDs from a monoexponential fit (Fig. S5C in the SM [37]). The relaxation pathways are depicted in the inset of Fig. 2(c) within the framework of the bulk one-particle picture. In this representation, photoexcited electrons and holes cool via intraband scattering toward the CBM and the VBM of the respective bands. Holes that cool into the lower VBM subsequently relax via inter-valence-band scattering to the upper VBM on a timescale of τ_{hole} . Translated to our quantum-confined system, these processes correspond to sequential exciton formation. Intraband cooling involves electrons and holes scattering among discrete states derived from the conduction band and lower valence bands, which eventually form exciton X2. Hole relaxation between states derived from the two uppermost valence bands corresponds to the inter-valence-band scattering, leading to the creation of exciton X1.

In a prior study on broad-emitting AgInS₂ QDs [46], two DT bleaching signals were reported, with the lower-energy feature exhibiting a delayed rise relative to the higher-energy one. While these observations were interpreted within a

theoretical framework developed for strongly confined CuInS₂ QDs [47], the AgInS₂ QDs investigated here operate in the weak-confinement regime and exhibit narrow free-exciton emission with high PLQY. Accordingly, we describe the optical transitions within the framework of the AgInS₂ bulk band structure, where the valence bands are intrinsically split due to crystal-field effects, and attribute the delayed rise to inter-valence-band hole relaxation. Building on this picture, we systematically investigate the size dependence of the hole relaxation.

Across all sizes, we observe a fast rise in exciton X2 bleach and two rise components for exciton X1, equivalent to the findings in 4.7 nm QDs (SM Sec. II A [37]). Interestingly, inter-valence-band hole relaxation exhibits a pronounced size dependence, with a faster relaxation in larger QDs, as shown in Fig. 2(c). Over the investigated size range, this trend can be described empirically by $\tau_{\text{hole}} \propto V^{-0.9 \pm 0.2}$, corresponding to a nearly inverse volume dependence of the hole relaxation time. We emphasize that this relation serves as a qualitative parametrization of the observed trend, since the size dependence of the exciton-phonon scattering rate does not generally follow a universal analytic scaling with QD size

[10]. The accelerated hole relaxation in larger QDs is not due to a size-dependent X1-X2 energy-phonon mismatch, owing to the similar X1-X2 splitting across all QD sizes (Fig. S4 in the SM [37]). Instead, it can be understood within phonon-scattering theory for confined systems [10,11], where increased state dispersion in larger QDs enhances exciton-phonon scattering efficiency. Within this picture, the slight deviation from a linear trend on the log-log scale observed in our data most likely reflects the crossover between two size limits. For larger QDs, the electronic structure progressively approaches the bulk limit, and the hole relaxation time is expected to saturate rather than continue decreasing indefinitely. Conversely, in smaller QDs, relatively stronger confinement enhances the discretization of the electronic states and reduces exciton-phonon scattering efficiency, resulting in a more rapid increase in the hole relaxation time. Such a trend stands in contrast to the Coulomb-mediated relaxation via energy transfer observed in III-V and II-VI QD systems, where electron states associated with small effective masses are sparsely distributed, while hole states with large effective masses are more densely spaced [12]. In such systems, a high-energy electron can efficiently transfer its excess energy to the hole, typically leading to faster relaxation as QD size decreases, which is opposite to our observation [14,48]. Once X2 is formed, the electron has already occupied the band-edge state. For the hole to relax via energy transfer, the energetic distance between X2 and X1 (~ 160 meV) would need to match the spacing between confined electron levels. This is highly unlikely in AgInS₂ QDs, given their small effective electron mass and the resulting widely spaced energy levels. The remaining hole must therefore relax via a phonon-mediated process to form X1. A qualitatively similar size-dependent carrier-relaxation slowdown has been shown for strongly confined FASnI₃ QDs [49]. Using their reported sizes and relaxation times, a scaling of $\tau_{\text{hole}} \propto V^{-2.9}$ can be inferred. This stronger size dependence may be associated with the stronger confinement and the large electronic energy spacing of ~ 300 meV in FASnI₃.

We now reveal biexciton transitions, induced by exciton X1, by temporally correlating the biexciton signal evolution with the hole relaxation. The corresponding transient at XX is depicted in Fig. 2(d) for 4.7 nm QDs. The signal initially rises negatively, then decays and turns positive. Importantly, the decay of this negative feature matches the hole relaxation dynamics shown in Fig. 2(b), highlighting that the temporal evolution of this feature is governed by hole relaxation, which is consistently observed in all QD sizes (Fig. S5B and SM Sec. IIA [37]). We therefore conclude that the biexciton-induced absorption originates predominantly from the X2 $\rightarrow$ X2X1 transition [19,50]. As the hole relaxes from X2 to X1, the biexciton-induced absorption to X1X1 spectrally overlaps with the bleach of X1, resulting in a net positive X1X1 signal. We model the transients in Fig. 2(e) to visualize the negative signal decay of the induced absorption amplitude (X2X1 $\rightarrow$ X1X1). While induced absorption to X1X1 persists as long as exciton X1 remains populated [24], the rising positive X1 bleach compensates for the negative induced X1X1 absorption [19].

Our assignment differs from earlier DT studies on broad-emitting AgInS₂ QDs, where carrier dynamics involve

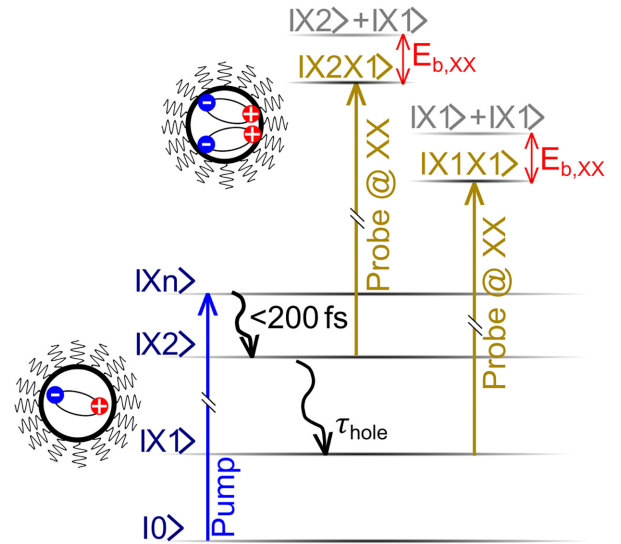


FIG. 3. Illustration of different exciton levels (X1, X2, and higher-energy exciton Xn), and biexciton levels (X1X1 and X2X1) in AgInS₂ QDs. The pump- and probe-induced transitions are depicted by blue and brown arrows, respectively. The biexciton levels are reduced by the biexciton binding energy ($E_{b,XX}$), relative to the sum of the two individual exciton levels.

sub-band-gap defect states [32,51]. Specifically, an induced absorption feature has been attributed to a probe-induced biexciton originating from antisite defect levels [32]. On the contrary, we observe a direct temporal correlation between the intrinsic hole relaxation and the XX signal consistently across all QD sizes, suggesting an intrinsic excitonic origin of the induced absorption feature. Furthermore, the amplitude of the induced absorption scales with excitation fluence and persists at long pump-probe delay times (>2000 ps with $\langle N \rangle \approx 1.7$, Fig. S7 in the SM [37]), consistent with biexciton-induced absorption rather than a defect-related origin.

We estimate the biexciton binding energy from Gaussian decomposition of the DT spectra for different-sized QDs (SM Sec. IIA [37]). These binding energies correspond to the X2X1 biexciton and range from 62 to 118 meV, indicating a general tendency toward larger values with decreasing QD size. For the X1X1 biexciton, a comparable binding energy is expected as the exciton states involve the same CBM. A larger biexciton binding energy in smaller QDs arises from a stronger spatial overlap of the exciton wavefunctions, which enhances the Coulomb interaction and thus increases the biexciton binding energy [15,16]. In comparison, confined excitons in Pb-halide perovskites are reported to exhibit a biexciton binding energy of 11–100 meV and in CdSe of up to 33 meV [21,23,25,28].

The overall excited-state dynamics are summarized schematically in Fig. 3, which depicts the single and biexciton levels. The latter are reduced by the biexciton binding energy compared to the sum of the two individual exciton energies. Following excitation by the pump pulse, high-energy excitons rapidly scatter to the X2 state (composed of electrons derived from the CBM and holes derived from the lower VBM), from which the probe induces the X2 $\rightarrow$ X2X1 biexciton transition. As the hole relaxes to the lowest state,

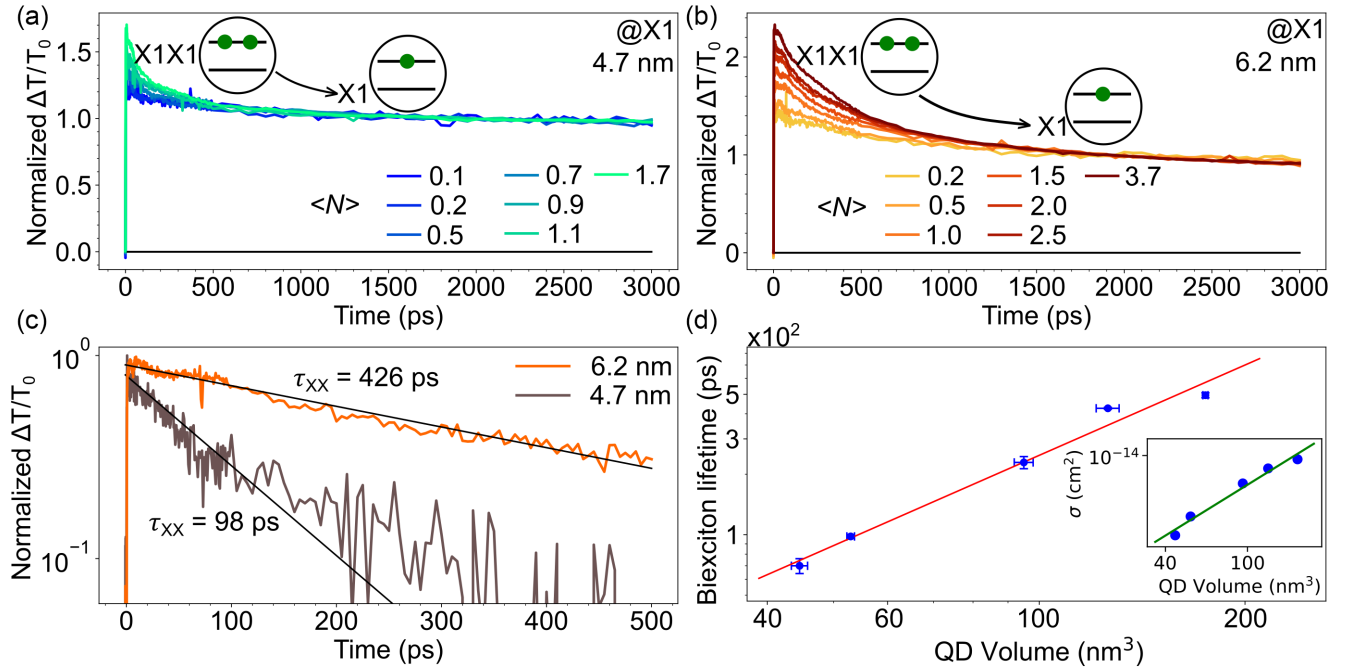


FIG. 4. (a),(b) DT decay curves of 4.7 nm QDs (a) and 6.2 nm QDs (b) for various $\langle N \rangle$ at the exciton X1 bleach [Panel (a), 565 nm; panel (b), 602 nm] upon 400 nm excitation. The transients are normalized at delay times >2500 ps. The schematic in the inset shows the transition from a biexciton to an exciton via biexciton decay. (c) The isolated averaged biexciton decay from (a) and (b) in logarithmic scale for 4.7 nm QDs in brown and 6.2 nm QDs in orange, yielding the biexciton decay time τ_{XX} . (d) Logarithmic-scale plot of size-dependent biexciton decay. The inset depicts the logarithmic-scale plot for the absorption cross section at 400 nm.

exciton X1 (composed of band-edge electrons and holes) is formed, and the population of X2 is depleted. Consequently, the X2X1 transition vanishes, and biexciton formation shifts to the $X1 \rightarrow X1X1$ transition. We note that transitions from higher-energy excitons X_n and X2 to higher biexciton states such as $X2X2$ and X_nX2 are also possible, as indicated by the weak negative signal below exciton X2 in Fig. 2(a) at very early delay times (<50 fs). In addition, formation of the X1X2 biexciton from exciton X1 may occur. However, these transitions predominantly overlap spectrally with the state-filling signals of excitons X2 and X1. These results establish a detailed understanding of the size-dependent sequential exciton relaxation and biexciton-formation pathways, highlighting the role of confinement in governing hole relaxation times in AgInS₂ QDs.

To understand multiexciton decay processes, we perform fluence-dependent DT measurements on the different-sized AgInS₂ QDs. Figures 4(a) and 4(b) show representative bleach transients of exciton X1 for 4.7 and 6.2 nm QDs, respectively, at various excitation fluences. The excitation fluences correspond to different average excitation numbers per dot ($\langle N \rangle$), determined by Poisson statistics (Figs. S12D and S13D in the SM [37]). The decay traces in Figs. 4(a) and 4(b) are normalized at delay times >2500 ps. For both QD sizes, the transients show identical late-time behavior across excitation fluences, independent of the initial excitation density. Thus, we attribute this regime to single-exciton decay. At early delay times, however, additional decay components emerge due to multiexciton interactions. Notably, the multiexciton decay in the 6.2 nm QDs [Fig. 4(b)] is slower than in the smaller 4.7 nm QDs [Fig. 4(a)]. To isolate the multiexciton

contribution, we subtract the single-exciton response obtained under low-fluence excitation. The resulting transients display monoexponential decay curves with similar decay dynamics across $\langle N \rangle$ (Figs. S12C and S13C in the SM [37]), confirming that the multiexciton dynamics are dominated by a biexciton decay. Figure 4(c) combines these results, showing average biexciton decay times of (98 ± 3) ps for 4.7 nm QDs and (426 ± 15) ps for 6.2 nm QDs. To evaluate the biexciton lifetime across the full-size series, we plot the extracted biexciton lifetimes in Fig. 4(d) (see SM Sec. II B for more details [37]). The biexciton decay time scales as $\tau_{XX} \propto V^{1.5 \pm 0.1}$ with QD volume (V), revealing a strong size dependence of the biexciton decay, which is consistent with trends reported for intrinsic biexciton recombination in established QD systems [26,29]. This behavior indicates a reduced efficiency of nonradiative biexciton recombination in larger QDs, leading to longer decay times. In contrast, trap-assisted Auger recombination exhibits a characteristic sub-linear volume dependence ($\tau \propto V^{0.67}$) [52]. The inset of Fig. 4(d) shows a nearly linear volume scaling of the absorption cross-section ($\sigma \propto V^{0.9 \pm 0.1}$) at 400 nm. This result indicates that AgInS₂ QDs possess a light absorption efficiency comparable to that of well-established Pb- and Cd-based QD systems at 400 nm (3.1 eV) [28,53].

The smaller AgInS₂ QDs exhibit decay times comparable to those of 11 nm Pb-halide perovskite QDs and 5 nm CdSe QDs [23,25,28]. In such 0D systems, nonradiative EEA between coulombically bound excitons or Auger recombination involving uncorrelated carriers, respectively, dominate the biexciton decay dynamics. In the former, one exciton recombines nonradiatively and transfers its energy to a second exciton, promoting it to a higher-lying state [53]. In the latter,

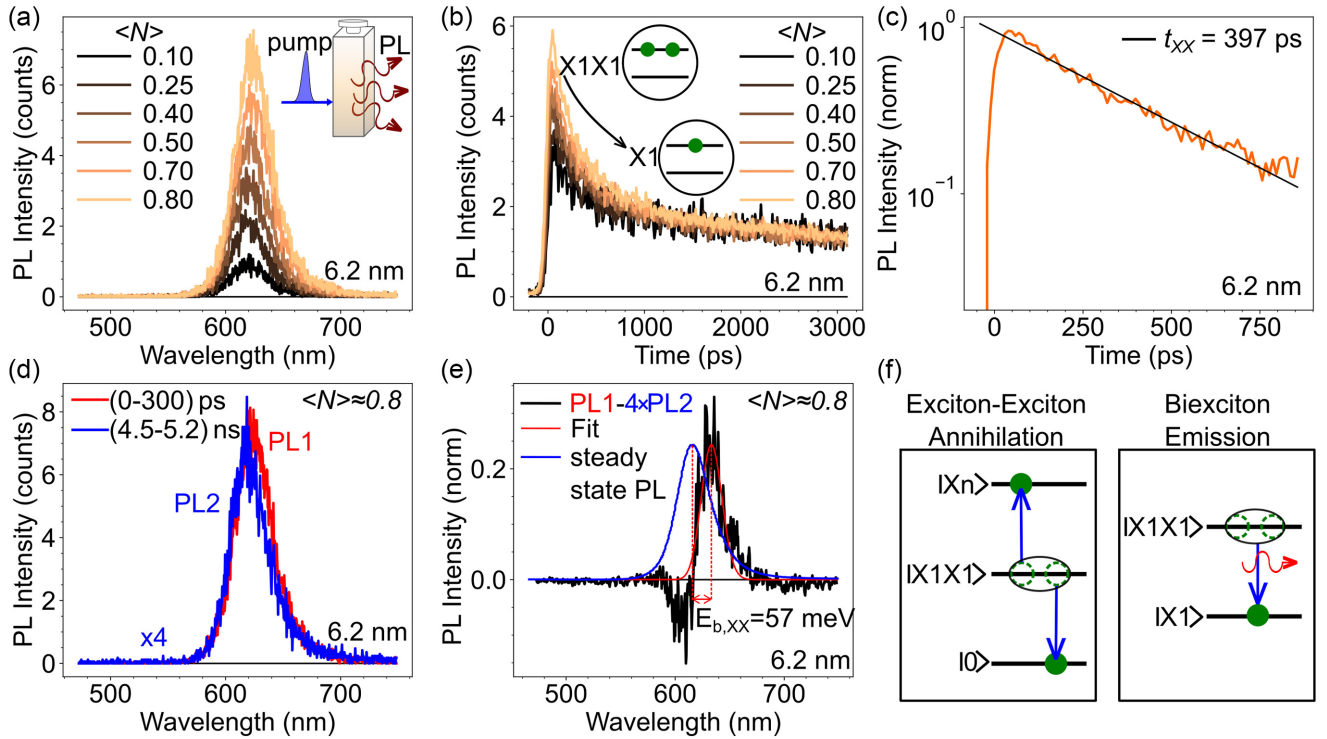


FIG. 5. (a) PL spectra of 6.2 nm QDs, temporally averaged over the first 400 ps at various $\langle N \rangle$. (b) PL decay curves, normalized at decay times >2500 ps at different excitation scenarios. The initial fast decay is schematically represented in the inset by a biexciton-to-exciton decay. (c) The extracted averaged biexciton decay for different curves in (b) in a logarithmic scale, revealing the biexciton decay time τ_{xx} . (d) Temporally averaged PL spectra at the biexciton-dominated regime PL1 in red and at the single exciton regime PL2 in blue for $\langle N \rangle \approx 0.8$. The blue spectrum PL2 is scaled by a factor of 4. (e) The difference of PL1 and PL2 from (d) in black, its Gaussian fit in red, and the steady-state PL spectrum in blue. The biexciton binding energy $E_{b,xx}$ is presented. (f) Schematic of the competing decay mechanisms: Nonradiative exciton-exciton annihilation on the left and radiative biexciton-to-exciton decay on the right.

the recombining electron-hole pair transfers its energy to a third carrier [26]. Accordingly, stronger quantum confinement in smaller AgInS₂ QDs enhances exciton-exciton overlap and additionally relaxes momentum conservation, leading to efficient nonradiative EEA. On the contrary, in larger AgInS₂ QDs, the exciton wave functions are comparably more delocalized, and momentum conservation increasingly restricts the annihilation process [26]. Consequently, EEA is less efficient, resulting in a longer biexciton decay time. The relatively long lifetime in this case raises the question of whether the decay is purely nonradiative or contains a radiative component.

To clarify the involvement of biexciton emission, we perform intensity-dependent PL lifetime measurements on large 6.2 nm AgInS₂ QDs using a streak camera. Figure 5(a) shows the intensity-dependent PL spectra, temporally averaged over the first 400 ps, which display a narrow emission linewidth. The spectrally integrated PL decays are presented in Fig. 5(b) for various $\langle N \rangle$ (determined by Poisson statistics, Fig. S17 in the SM [37]). As in the pump-probe measurements, the traces converge at long decays (>2500 ps), indicating single-exciton recombination, while additional fast components appear at early times. Subtracting the single-exciton contribution isolates a faster decay, which is mono-exponential across excitation fluences (Fig. S18C in the SM [37]). The averaged decay [Fig. 5(c)] yields a time constant of (397 ± 8) ps, matching the biexciton lifetime determined from pump-probe

spectroscopy. Hence, the time-resolved PL dynamics are governed by biexciton and single-exciton decays.

To investigate spectral signatures of the emission, we compare the PL spectrum within the biexciton-dominated regime (temporally averaged within <300 ps, PL1) with that of the single-exciton regime (temporally averaged within 4.5–5.2 ns, PL2) in Fig. 5(d). Surprisingly, the PL1 is redshifted relative to PL2, revealing biexciton emission ($X1X1 \rightarrow X1$), which has not been reported previously in the I-III-VI QD material class. Due to the biexciton binding energy, the biexciton emission (PL1) occurs at longer photon wavelengths than the single-exciton emission (PL2). Importantly, at lower excitation fluences, we do not observe this spectral shift (Fig. S19 in the SM [37]), consistent with biexciton emission appearing only under high-fluence excitation. To estimate the biexciton binding energy from our streak measurements, we qualitatively isolate the biexciton contribution by subtracting spectrum PL2 from PL1 and compare the result with the steady-state PL [Fig. 5(e)] [23,54]. From this difference, a biexciton binding energy of $E_{b,xx} = (57 \pm 5)$ meV is derived, in good agreement with the value obtained from pump-probe experiments ($E_{b,xx} = 62 \pm 15$ meV). Figure 5(f) schematically summarizes the competing processes of EEA and biexciton emission. In larger 6.2 nm QDs, the reduced annihilation probability, stemming from weaker confinement of excitons, permits partial radiative biexciton

emission. On the other hand, fast biexciton decay is dominated by non-radiative EEA in smaller QDs.

III. CONCLUSIONS

In this work, we systematically study bright, narrow green-to-red-emitting AgInS₂ QDs with emission efficiencies up to 56%. By tuning the QD size, we deduce a sizing curve and optically explore exciton and biexciton dynamics, as well as exciton-exciton interactions across all sizes, that depend on the degree of confinement. We find that the inter-valence-band hole relaxation involving exciton X2 and X1 accelerates with increasing QD size. Our results reveal the complex landscape of exciton-to-biexciton transitions, demonstrating that the biexciton signal originates from the X2 → X2X1 transition before hole relaxation completes to form X1. Biexciton dynamics are systematically investigated, revealing that the biexciton decay time scales with QD size. The short sub-100 ps biexciton lifetime in smaller QDs is primarily governed by rapid EEA, whereas in larger QDs, the annihilation rate decreases and radiative biexciton emission emerges under

high fluence excitation. Together, these ultrafast spectroscopic measurements establish a detailed, fundamental picture of exciton and biexciton dynamics in I-III-VI QDs, providing insights relevant to the design of next-generation QD-based light-emitting and energy-harvesting devices.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Bavarian State Ministry of Science, Research, and the Arts, as well as LMU Munich, through the grant “Solar Technologies go Hybrid (SolTech).” We also extend our gratitude to local research centers, including the Center of Nanoscience (CeNS), for fostering effective networking opportunities.

The authors declare no conflict of interest.

DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

- [1] T. Uematsu, K. Wajima, D. K. Sharma, S. Hirata, T. Yamamoto, T. Kameyama, M. Vacha, T. Torimoto, and S. Kuwabata, Narrow band-edge photoluminescence from AgInS₂ semiconductor nanoparticles by the formation of amorphous III–VI semiconductor shells, *NPG Asia Mater.* **10**, 713 (2018).
- [2] L. Yang *et al.*, I–III–VI quantum dots and derivatives: Design, synthesis, and properties for light-emitting diodes, *Nano Lett.* **23**, 2443 (2023).
- [3] H. J. Lee *et al.*, Coherent heteroepitaxial growth of I–III–VI₂ Ag(In, Ga)S₂ colloidal nanocrystals with near-unity quantum yield for use in luminescent solar concentrators, *Nat. Commun.* **14**, 3779 (2023).
- [4] D. Yan, H. Chen, L. Zhang, Y. Luo, Y. Dong, Y. Zou, and H. Zeng, Intrinsic defect self-compensation enables spectrum narrowing of uniform alloyed Ag–In–Ga–S quantum dots, *ACS Energy Lett.* **10**, 3755 (2025).
- [5] S. Park, B. J. Kim, W. H. Jung, K. H. Lee, H. Lee, and J. Lim, Suppressing tail emission from AgIn_{1-x}Ga_xS₂/AgGaS₂ quantum dots by GaI₃-assisted interface reinforcement, *ACS Nano* **19**, 26831 (2025).
- [6] A. Saha, M. Cervino, H. Roshan, R. Hübner, A. Wrzesińska-Lashkova, C. Steinbach, Y. Vaynzof, F. Di Stasio, and V. Lesnyak, RoHS-Compliant, Cu–Zn–In–Se-Based core/multi-shell quantum dots with efficient and tunable short-wave infrared emission, *Adv. Funct. Mater.* **36**, e17605 (2025).
- [7] A. Saha, S. Basel, C. Rivaux, D. Aldakov, and P. Reiss, AgGaS₂/Ga₂S₃ quantum dots exhibiting efficient narrow blue emission, *J. Mater. Chem. C* **13**, 19017 (2025).
- [8] J. Bai, Y. Han, T. Zhang, L. Wang, K. Qiu, C. Cai, B. Xu, X. Jin, and Q. Li, Highly luminescent green-emitting AgInS₂/ZnS quantum dots enabled by controlling Zn ion exchange for white light-emitting diodes, *J. Alloys Compd.* **1036**, 181929 (2025).
- [9] S. V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals*, Cambridge Studies in Modern Optics (Cambridge University Press, Cambridge, 1998).
- [10] U. Bockelmann and G. Bastard, Phonon scattering and energy relaxation in two-, one-, and zero-dimensional electron gases, *Phys. Rev. B* **42**, 8947 (1990).
- [11] J. Urayama, T. B. Norris, J. Singh, and P. Bhattacharya, Observation of phonon bottleneck in quantum dot electronic relaxation, *Phys. Rev. Lett.* **86**, 4930 (2001).
- [12] A. L. Efros, V. A. Kharchenko, and M. Rosen, Breaking the phonon bottleneck in nanometer quantum dots: Role of Auger-like processes, *Solid State Commun.* **93**, 281 (1995).
- [13] T. S. Sosnowski, T. B. Norris, H. Jiang, J. Singh, K. Kamath, and P. Bhattacharya, Rapid carrier relaxation in In_{0.4}Ga_{0.6}As/GaAs quantum dots characterized by differential transmission spectroscopy, *Phys. Rev. B* **57**, R9423 (1998).
- [14] V. I. Klimov, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Electron and hole relaxation pathways in semiconductor quantum dots, *Phys. Rev. B* **60**, 13740 (1999).
- [15] T. Takagahara, Biexciton states in semiconductor quantum dots and their nonlinear optical properties, *Phys. Rev. B* **39**, 10206 (1989).
- [16] Y. Z. Hu, S. W. Koch, M. Lindberg, N. Peyghambarian, E. L. Pollock, and F. F. Abraham, Biexcitons in semiconductor quantum dots, *Phys. Rev. Lett.* **64**, 1805 (1990).
- [17] Y. Z. Hu, M. Lindberg, and S. W. Koch, Theory of optically excited intrinsic semiconductor quantum dots, *Phys. Rev. B* **42**, 1713 (1990).
- [18] K. I. Kang, A. D. Kepner, S. V. Gaponenko, S. W. Koch, Y. Z. Hu, and N. Peyghambarian, Confinement-enhanced biexciton binding energy in semiconductor quantum dots, *Phys. Rev. B* **48**, 15449 (1993).
- [19] V. Klimov, S. Hunsche, and H. Kurz, Biexciton effects in femtosecond nonlinear transmission of semiconductor quantum dots, *Phys. Rev. B* **50**, 8110 (1994).
- [20] F. Gindele, U. Woggon, W. Langbein, J. M. Hvam, K. Leonardi, D. Hommel, and H. Selke, Excitons, biexcitons, and phonons in

- ultrathin CdSe/ZnSe quantum structures, *Phys. Rev. B* **60**, 8773 (1999).
- [21] M. Achermann, J. A. Hollingsworth, and V. I. Klimov, Multiexcitons confined within a subexcitonic volume: Spectroscopic and dynamical signatures of neutral and charged biexcitons in ultrasmall semiconductor nanocrystals, *Phys. Rev. B* **68**, 245302 (2003).
- [22] B. Patton, W. Langbein, and U. Woggon, Trion, biexciton, and exciton dynamics in single self-assembled CdSe quantum dots, *Phys. Rev. B* **68**, 125316 (2003).
- [23] J. A. Castañeda *et al.*, Efficient biexciton interaction in perovskite quantum dots under weak and strong confinement, *ACS Nano* **10**, 8603 (2016).
- [24] A. Barfüßer, S. Rieger, A. Dey, A. Tosun, Q. A. Akkerman, T. Debnath, and J. Feldmann, Confined excitons in spherical-like halide perovskite quantum dots, *Nano Lett.* **22**, 8810 (2022).
- [25] A. Barfüßer, J. Feldmann, and Q. A. Akkerman, Biexcitonic optical gain in CsPbBr₃ quantum dots, *ACS Photon.* **11**, 5350 (2024).
- [26] V. I. Klimov, Spectral and dynamical properties of multiexcitons in semiconductor nanocrystals, *Annu. Rev. Phys. Chem.* **58**, 635 (2007).
- [27] F. García-Santamaría, S. Brovelli, R. Viswanatha, J. A. Hollingsworth, H. Htoon, S. A. Crooker, and V. I. Klimov, Breakdown of volume scaling in Auger recombination in CdSe/CdS heteronanocrystals: The role of the core-shell interface, *Nano Lett.* **11**, 687 (2011).
- [28] N. S. Makarov, S. Guo, O. Isaienko, W. Liu, I. Robel, and V. I. Klimov, Spectral and dynamical properties of single excitons, biexcitons, and trions in cesium-lead-halide perovskite quantum dots, *Nano Lett.* **16**, 2349 (2016).
- [29] Y. Li, X. Luo, T. Ding, X. Lu, and K. Wu, Size- and halide-dependent Auger recombination in lead halide perovskite nanocrystals, *Angew. Chem. Int. Ed.* **59**, 14292 (2020).
- [30] J. G. Mann, E. Kostyurina, M. Döblinger, B. Nickel, J. Feldmann, and S. Ghimire, Diminishing surface defects in silver indium sulfide quantum dots enables bandgap-excitonic characteristics, *Adv. Opt. Mater.* **13**, e00434 (2025).
- [31] T. Debnath, S. Maiti, P. Maity, and H. N. Ghosh, Subpicosecond exciton dynamics and biexcitonic feature in colloidal CuInS₂ nanocrystals: Role of In-Cu antisite defects, *J. Phys. Chem. Lett.* **6**, 3458 (2015).
- [32] J. Dana, T. Debnath, and H. N. Ghosh, Involvement of sub-bandgap states in subpicosecond exciton and biexciton dynamics of ternary AgInS₂ nanocrystals, *J. Phys. Chem. Lett.* **7**, 3206 (2016).
- [33] J. Sun, M. Ikezawa, X. Wang, P. Jing, H. Li, J. Zhao, and Y. Masumoto, Photocarrier recombination dynamics in ternary chalcogenide CuInS₂ quantum dots, *Phys. Chem. Chem. Phys.* **17**, 11981 (2015).
- [34] G. Yang, S. Shi, X. Zhang, S. Zhou, D. Liu, Y. Liang, Z. Chen, and G. Liang, Ultrafast photophysical process of biexciton Auger recombination in CuInS₂ quantum dots studied by transient-absorption spectroscopy, *Opt. Express* **29**, 9012 (2021).
- [35] C. J. Stolle, R. D. Schaller, and B. A. Korgel, Efficient carrier multiplication in colloidal CuInSe₂ nanocrystals, *J. Phys. Chem. Lett.* **5**, 3169 (2014).
- [36] J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, International Series in the Science of the Solid State Vol. 7 (Elsevier, Oxford, United Kingdom, 1975).
- [37] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.114.125420> for sample preparation, experimental methods, characterization and optical steady-state experiments (Sec. I), supporting data on the single exciton regime, and complete size series including all fits in the single exciton regime (Sec. II A) and the multiexciton regime (Secs. II B and II C), which includes Ref. [55].
- [38] J. L. Shay, B. Tell, L. M. Schiavone, H. M. Kasper, and F. Thiel, Energy bands of AgInS₂ in the chalcopyrite and orthorhombic structures, *Phys. Rev. B* **9**, 1719 (1974).
- [39] B. J. Bohn, Y. Tong, M. Gramlich, M. Ling Lai, M. Döblinger, K. Wang, R. L. Z. Hoyer, P. Müller-Buschbaum, S. D. Stranks, A. S. Urban, *et al.*, Boosting tunable blue luminescence of halide perovskite nanoplatelets through postsynthetic surface trap repair, *Nano Lett.* **18**, 5231 (2018).
- [40] D. Huang and C. Persson, Photocatalyst AgInS₂ for active overall water-splitting: A first-principles study, *Chem. Phys. Lett.* **591**, 189 (2014).
- [41] J. Liu and E. Hua, Electronic structure and absolute band edge position of tetragonal AgInS₂ photocatalyst: A hybrid density functional study, *Mater. Sci. Semicond. Proc.* **40**, 446 (2015).
- [42] C. Delerue, G. Allan, and M. Lannoo, Theoretical aspects of the luminescence of porous silicon, *Phys. Rev. B* **48**, 11024 (1993).
- [43] G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, F. Huisken, B. Kohn, and V. Paillard, Photoluminescence properties of silicon nanocrystals as a function of their size, *Phys. Rev. B* **62**, 15942 (2000).
- [44] B. P. Falcão, J. P. Leitão, M. R. Soares, J. Rodrigues, L. Ricardo, H. Águas, R. Martins, and R. N. Pereira, Size-dependent critical transition in the origin of light emission from core-shell Si-SiO₂ nanoparticles, *J. Mater. Chem. C* **8**, 9012 (2020).
- [45] S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, Theory of the linear and nonlinear optical properties of semiconductor microcrystallites, *Phys. Rev. B* **35**, 8113 (1987).
- [46] M. L. Zaffalon, V. Pinchetti, A. Camellini, S. Vikulov, C. Capitani, B. Bai, M. Xu, F. Meinardi, J. Zhang, L. Manna, *et al.*, Intrinsic and extrinsic exciton recombination pathways in AgInS₂ colloidal nanocrystals, *Energy Mater. Adv.* **2021**, 1959321 (2021).
- [47] A. Shabaev, M. J. Mehl, and A. L. Efros, Energy band structure of CuInS₂ and optical spectra of CuInS₂ nanocrystals, *Phys. Rev. B* **72**, 035431 (2005).
- [48] P. Yu, J. M. Nedeljkovic, P. A. Ahrenkiel, R. J. Ellingson, and A. J. Nozik, Size dependent femtosecond electron cooling dynamics in CdSe quantum rods, *Nano Lett.* **4**, 1089 (2004).
- [49] L. Dai, Z. Deng, F. Auras, H. Goodwin, Z. Zhang, J. C. Walmsley, P. D. Bristowe, F. Deschler, and N. C. Greenham, Slow carrier relaxation in tin-based perovskite nanocrystals, *Nat. Photon.* **15**, 696 (2021).
- [50] V. I. Klimov and D. W. McBranch, Femtosecond 1P-to-1S electron relaxation in strongly confined semiconductor nanocrystals, *Phys. Rev. Lett.* **80**, 4028 (1998).
- [51] K. Yu, Y. Yang, J. Wang, X. Tang, Q.-H. Xu, and G. P. Wang, Ultrafast carrier dynamics and third-order nonlinear optical properties of AgInS₂/ZnS nanocrystals, *Nanotechnology* **29**, 255703 (2018).
- [52] A. W. Cohn, A. M. Schimpf, C. E. Gunthardt, and D. R. Gamelin, Size-dependent trap-assisted auger recombination

- in semiconductor nanocrystals, [Nano Lett. **13**, 1810 \(2013\)](#).
- [53] M. Gramlich, B. J. Bohn, Y. Tong, L. Polavarapu, J. Feldmann, and A. S. Urban, Thickness-dependence of exciton–exciton annihilation in halide perovskite nanoplatelets, [J. Phys. Chem. Lett. **11**, 5361 \(2020\)](#).
- [54] G. Nagamine, J. O. Rocha, L. G. Bonato, A. F. Nogueira, Z. Zaharieva, A. A. R. Watt, C. H. de Brito Cruz, and L. A. Padilha, Two-photon absorption and two-photon-induced gain in perovskite quantum dots, [J. Phys. Chem. Lett. **9**, 3478 \(2018\)](#).
- [55] B. Hammouda, A new Guinier–Porod model, [J. Appl. Cryst. **43**, 716 \(2010\)](#).