Review

Buyang Yu, Chunfeng Zhang*, Lan Chen, Zhengyuan Qin, Xinyu Huang, Xiaoyong Wang and Min Xiao

Ultrafast dynamics of photoexcited carriers in perovskite semiconductor nanocrystals

<https://doi.org/10.1515/nanoph-2020-0681>

Received December 30, 2020; accepted February 4, 2021;
published online February 19, 2021

Abstract: Perovskite semiconductor nanocrystals have emerged as a promising family of materials for optoelectronic applications including light-emitting diodes, lasers, light-to-electricity converters and quantum light emitters. The performances of these devices are fundamentally dependent on different aspects of the excited-state dynamics in nanocrystals. Herein, we summarize the recent progress on the photoinduced carrier dynamics studied by a variety of time-resolved spectroscopic methods in perovskite nanocrystals. We review the dynamics of carrier generation, recombination and transport under different excitation densities and photon energies to show the pathways that underpin the photophysics for light-emitting diodes and solar cells. Then, we highlight the up-to-date spin dynamics and coherent exciton dynamics being manifested with the exciton fine levels in perovskite semiconductor nanocrystals which are essential for potential applications in quantum information technology. We also discuss the controversial results and the possible origins yet to be resolved. In-depth study toward a comprehensive picture of the excited-state dynamics in perovskite nanocrystals may provide the key knowledge of the device operation mechanism, enlighten the direction

for device optimization and stimulate the adventure of new conceptual devices.

Keywords: coherent dynamics; exciton dynamics; perovskite nanocrystals; spin dynamics; ultrafast spectroscopy.

1 Introduction

Lead halide compounds adopting CaTiO_3 -like ABX_3 structures have emerged as a family of semiconductors promising for optoelectronic applications. These perovskite semiconductors exhibit strong light absorption [1–3] and excellent charge transport properties [4–6], enabling highly efficient light-to-electricity conversion for device applications such as solar cells [7, 8] and photodetectors [9–12]. The bandgaps of perovskite semiconductors can be further tuned by engineering elements at the B and X sites [13–15]. The tandem solar cells by integrating devices with perovskite semiconductors of different bandgaps may largely extend the spectral range of light harvesting [7, 16, 17]. Perovskite semiconductors also exhibit efficient light emission, which has been successfully used to demonstrate light-emitting diodes (LEDs) [18–20] and lasers [21, 22].

Since 2015, nanocrystals of perovskite semiconductors have been proposed to enhance the light emitting performance for LED applications [23, 24]. In nanocrystals with sizes comparable to or smaller than the Bohr radii, the electron and hole wavefunctions are spatially confined [25–27]. Such a quantum confinement effect stabilizes the excitons in semiconductor nanocrystals. Benefiting from the excitonic effect, photoluminescence (PL) emissions from perovskite semiconductor nanocrystals typically exhibit narrow spectral bandwidths with relatively high quantum efficiencies [28–31]. The emission colors of perovskite semiconductor nanocrystals can be controlled by size and composition engineering with cost-effective approaches [23, 24, 32, 33]. These superior optical properties make perovskite semiconductor nanocrystals excellent candidates for potential applications in lasers [34–37], LEDs [24, 38–40], X-ray scintillators [41, 42] and luminescent solar concentrators [43, 44]. Moreover,

***Corresponding author: Chunfeng Zhang**, National Laboratory of Solid State Microstructures, School of Physics, Collaborative Innovation Center for Advanced Microstructures, Nanjing University, Nanjing 210093, China, E-mail: cfzhang@nju.edu.cn. <https://orcid.org/0000-0001-9030-5606>

Buyang Yu, Lan Chen, Zhengyuan Qin, Xinyu Huang and Xiaoyong Wang, National Laboratory of Solid State Microstructures, School of Physics, Collaborative Innovation Center for Advanced Microstructures, Nanjing University, Nanjing 210093, China, E-mail: byyu1996@qq.com (B. Yu), chenlanphy@163.com (L. Chen), 946929462@qq.com (Z. Qin), huangxinyu@smail.nju.edu (X. Huang), wxiaoyong@nju.edu.cn (X. Wang)

Min Xiao, Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA, E-mail: mxiao@uark.edu

perovskite semiconductor nanocrystals also exhibit excellent performances for solar cells whose power-conversion efficiencies lead the performances of nanocrystal-based solar cell devices [45, 46]. In addition, the excitonic transition in perovskite semiconductor nanocrystals has been recognized as a quantum two-level system being manifested with single photon emission, which can be potentially applied for quantum information technology [47, 48].

The performance of an optoelectrical device is highly relevant to the excited-state dynamics in semiconductors. For solar cells, the efficiency is fundamentally limited by the competition between the charge generation/collection and carrier recombination. It is critical to elucidate the charge carrier dynamics upon weak excitation of density comparable to sun light illumination. For LED applications, the interplay between the radiative and nonradiative recombination sets the overall efficiency. Particularly, the current-injected carriers are spin random while light emission is only allowed for the transitions from “bright” exciton states. It is important to uncover the dynamics involving excited states with different spin characters. For laser applications, optical gain induced by population inversion is typically generated upon high density excitation, which requires a clear picture for the many-body effects. For quantum light emission, it is essential to clarify the quantum dephasing process as well as the fine excitonic levels. In the last few years, time-resolved spectroscopic methods, such as ultrafast transient absorption (TA), time-resolved PL (TRPL), optical pump terahertz (THz) probe (OPTP) and two-dimensional electronic spectroscopy (2DES), together with single-particle and magneto-optical spectroscopic methods have been intensively applied to study different aspects of carrier dynamics in perovskite semiconductor nanocrystals [49–55]. The knowledge of excited-state dynamics provided by ultrafast spectroscopic studies is essential for understanding the underlying mechanism in perovskite-semiconductor-nanocrystal-based optoelectronic devices, which may also stimulate the exploration of new conceptual devices.

In this review, we highlight the excited-state dynamics in the ABX_3 -type perovskite semiconductor nanocrystals with the most widely studied cubic shapes. First, we review the dynamics of carrier generation and recombination under different excitation densities and photon energies. In the second part, we focus on the spin-related excited-state dynamics including exciton fine structures and spin depolarization processes. Then the recent studies on coherent dynamics are briefly reviewed. These studies reveal the picture of the excited-state dynamics of perovskite semiconductor nanocrystals and the underlying mechanism, and also open up opportunities to the broad

prospects of applications of perovskite semiconductor nanocrystals.

2 Carrier generation and recombination

Optical excitation creates electron-hole pairs as the start point of many optoelectronic responses in semiconductor nanocrystals. Due to size confinement, the electron-hole pair is typically formed as exciton in semiconductor nanocrystals. For nanocrystals of perovskite semiconductors (Figure 1(a)), the excitonic resonance can be easily tailored by nanocrystal size (Figure 1(b)) and composition (Figure 1(c)). Due to the exciton-exciton and exciton-structure imperfection interactions, some bound complexes, e.g., trions and biexcitons, may be also excited in perovskite nanocrystals. These different excited species created upon optical excitations of different photon energies and intensities may undergo different de-excitation pathways as shown in Figure 1(d). These excited-states dynamics on different time scale are ultimately responsible for the performance of optoelectrical devices.

2.1 Charge carrier dynamics upon weak excitation

2.1.1 Excitons and trions

In semiconductor nanocrystals, photon-induced optical transitions can generate excitons which refer to the Coulomb-interaction-mediated neutral bound complexes of electrons and holes. Due to the spatial-confinement-induced enhanced overlap of electron and hole wavefunctions, semiconductor nanocrystals exhibit obvious excitonic characteristics [26]. The relaxation, interaction and recombination dynamics of these excitons are strongly dependent on the composite and the nanocrystal size. TRPL spectroscopic measurements are commonly used to characterize the lifetime parameters of exciton recombination. In combination with quantum yields of PL measurements, TRPL spectra can be used to estimate the radiative and nonradiative recombination rates. In perovskite nanocrystals, the recombination lifetimes of band-edge excitons vary from 1 to 75 ns at room temperature [23, 24, 56].

The bandgap of perovskite semiconductor nanocrystals can be tuned to cover almost the entire visible range with high PL quantum efficiencies by changing halide anion using cost-effective wet chemical approaches [23, 24, 33]. The radiative recombination lifetime of CsPbX_3

Figure 1: (a) Schematic diagram of the perovskite semiconductor with ABX_3 structure, where A is an organic or alkali-metal cations (e.g., MA^+ , FA^+ or Cs^+), B is a divalent cation (e.g., Pb^{2+}) and X is a halide anion (e.g., Cl^- , Br^- or I^-). (b) Absorption and PL spectra of $CsPbBr_3$ nanocrystals with different sizes. (c) Absorption and PL spectra of perovskite semiconductor nanocrystals with different halide compositions. (d) Dynamics of photoexcited carriers in a perovskite semiconductor nanocrystal discussed in this review. A photoexcited electron-hole pair loses the excess energy through the process of phonon emission and/or carrier multiplication. PL emission is mainly contributed by the radiative recombination of relaxed electron-hole pair that competes with the carrier trapping and other non-radiative channels. The recombination dynamics of trions and biexcitons are strongly affected by Auger recombination induced by many-body interaction. (b) and (c) Reproduced with permission [23]. Copyright 2015, American Chemical Society.

nanocrystal changes from 1 to 29 ns by changing halide elements of X from Cl, Br to I [23]. The composition dependence of the recombination lifetime is likely caused by the gap-dependent oscillation strength of interband transitions. In principle, these nanocrystals, with highly efficient PL emission covering broad spectral range, are applicable for color-tunable light-emitting devices. Nevertheless, perovskite nanocrystals with mixed halides suffer from the phase segregation under persistent irradiation even at single nanocrystal level [57], which require to be appropriately addressed.

Manipulating nanocrystal size is another effective strategy to detune the light emission color of perovskite semiconductor nanocrystals. The Bohr radii and typical binding energies of excitons for perovskite semiconductors are on the orders of 1 nm and 10 s meV within the effective

mass approximation (e.g., $CsPbCl_3$ (~2.5 nm, ~75 meV), $CsPbBr_3$ (~3.5 nm, ~40 meV) and $CsPbI_3$ (~6.0 nm, ~20 meV)) [23]. The quantum confinement effect is significant in nanocrystals with sizes comparable to or smaller than the exciton Bohr radii. With decreasing size, PL emission from semiconductor nanocrystals may exhibit significantly blue shift of emission energy. The spatial overlaps of electron and hole wavefunctions are enhanced in small nanocrystals which strongly modifies the rates of interband recombination [32, 58]. Yao et al. [58] found that the PL lifetime is shortened from 75 to 15 ns in $CsPbI_3$ nanocrystals when the nanocrystal size decreases from 14 to 5 nm. Initially, perovskite nanocrystals with smaller sizes are relatively unstable, which has been recently addressed by optimizing the growth temperature [32] and/or doping with divalent metal cations such as Sr^{2+} [58] and

Zn²⁺ [59]. These stable nanocrystals exhibit high PL quantum yields which have successfully been adopted for efficient LED applications [40, 58, 60].

Ultrafast TA spectroscopies have also been widely applied to investigate the excited-state dynamics in perovskite nanocrystals. TA spectroscopic measurements allow to probe the nonemissive states with a subpicosecond time resolution. TA spectra usually consist of the photoinduced bleaching (PIB) features caused by the ground-state bleaching and stimulated emission and the excited-state absorption (ESA) features due to transition to higher energy levels. Figure 2(a) shows the TA spectra of CsPbI₃ nanocrystals reported by Yumoto and coworkers [61]. The PIB peaks around 1.91 and 2.01 eV match with the steady-state absorption peaks in Figure 2(b) which are ascribed to the optical transitions to the discrete states of excitons induced by the quantum confinement effect. The temporal dynamics under low excitation fluence corresponds to the exciton decay process. ESA features can be found on both sides of the excitonic bleach peak, which are contributed by the transitions from the exciton state to the higher-level states associated to many-body effect as discussed later.

The existence of trap states may lead to an additional temporal component of exciton recombination under low fluence excitation [64]. In perovskite semiconductor nanocrystals, previous studies have shown that these trap states are shallow in nature that can trap electrons or holes

within 6–50 ps [64, 65]. Due to the symmetry breaking at the surface of the nanocrystals, the formed surface trap centers are found to be one of the primary sources to trap carriers. Therefore, the surface treatment by ligands or passivating agents is considered to play an essential role on the trap state density in perovskite semiconductor nanocrystals [28, 54, 66]. For example, by treating with trioctylphosphine as a solvent and ligand, the synthesized CsPbI₃ nanocrystals are reported to possess low trap-state density, which was confirmed by TA measurements that the fast recombination component is significantly suppressed if compared with the oleic acid/oleylamine-based nanocrystals [28]. Surface treatment has been established as an effective strategy to improve the performance of nanocrystal-based light-emitting devices. By proper surface managements, the external quantum efficiencies of perovskite nanocrystal-based LEDs have exceeded 12% [40] and 23% [67] for blue and green emissions.

These surface states may also lead to the formation of the trion which refers to the bound complex of two electrons (holes) and one hole (electron) (Figure 3(a)) [25]. The recombination of trion can be dominated by Auger recombination induced by a three-body interaction [68, 69]. In nanocrystals, the Auger process is markedly enhanced, which is attributed to the more easily satisfied conservation of energy and momentum in the quantum confined system [70, 71]. The rate of Auger recombination is scaled with the state occupation of electrons and holes [25]. Therefore, Auger recombination is generally much faster than the recombination process of single exciton [72, 73]. The Auger recombination of trion is considered to be responsible for the decreased PL efficiency and PL blinking for single nanocrystal emission [48, 74–76]. For ensemble nanocrystals, the trion recombination can be studied by TRPL and TA techniques. Makarov et al. [62] studied the recombination of trions in CsPbBr_{1.5}I_{1.5} nanocrystals by TRPL. They found the suppression of the fast component and the enhancement of the long-lived component under stirring, which is the signature of reduced trion recombination (Figure 3(b)) [25]. Yarita et al. [63] studied the recombination dynamics in CsPbBr₃ nanocrystals under different power pumps (Figure 3(c) and (d)). They analyzed the fluence-dependent carrier dynamics under the assumption of Poisson distributions with the average electron-hole pairs per nanocrystal. The characteristic lifetimes of decay component of exciton and biexciton recombination are characterized to be ~5.7 ns and ~40 ps, respectively. In addition to these two components, they observed that additional component with characteristic lifetime of ~190 ps is necessary to reproduce the dynamic curves, which actually is detectable under weak excitation

Figure 2: (a) The typical TA spectra of perovskite semiconductor nanocrystals. (b) The absorption spectrum and the corresponding second-order derivative of the same sample in (a). (a) and (b) Reproduced with permission [61]. Copyright 2018, American Chemical Society.

Figure 3: (a) Schematic of a positive trion (upper left), a negative trion (upper right) and an exciton (bottom) excited in a semiconductor nanocrystal. (b) TRPL spectra of the stirred (black) and static (red) solutions of CsPbBr_{1.5}I_{1.5} nanocrystals. Reproduced with permission [62]. Copyright 2016, American Chemical Society. (c) Power dependence of the TA curves in CsPbBr₃ nanocrystals monitored at the band-edge exciton bleach. (d) The amplitudes of the decay components of exciton, trion and biexciton versus the excitation photon fluence extracted from (c). (c) and (d) Reproduced with permission [63]. Copyright 2017, American Chemical Society.

of only 0.17 electron-hole pair per nanocrystal. Considering that most light-emitting devices work under current injection, the trion component should be carefully treated. Lately, the trion issue can be released by surface passivation. Nakahara et al. [77] studied the influence of surface passivation on trion recombination by TA in ensemble CsPbBr₃ nanocrystals. By treating with NaSCN as reported earlier [66], they found a decreased component of trion revealing the possibility of suppressing the formation of trion through postsynthetic surface modification.

2.1.2 Free carriers

For solar cells and photodetectors, the photoexcited excitons dissociate into free electrons and holes which are then collected by electrodes for light-to-electricity conversion [54]. Therefore, the generation and transport of the free carriers are essential. In the bulk materials of perovskite semiconductors, bipolar transport has been characterized with efficient and balanced electron/hole diffusion [4, 5, 78–81], exhibiting remarkably long carrier lifetime [82, 83], high carrier mobility and excellent defect tolerance [83, 84]. These exceptional transport properties have been attributed to the efficient charge separation induced by the ferroelectric domains [85], the charge carrier screening effect induced by large polaron formation along with the phonon glass character lattice [86] and the spin blockade effect induced by the strong spin-orbital interaction [87]. In perovskite nanocrystals, the small size strongly affects the

charge transport properties. In comparison with the polycrystalline films, the carrier mobility in perovskite nanocrystals is over one-order of magnitude reduced, which is one key factor that limits the overall efficiency of the nanocrystal-based solar cells.

THz spectroscopy, i.e., THz time-domain spectroscopic and OPTP measurements, has been established as a viable nonelectric-contact tool to study the charge transport in perovskite nanocrystal systems. By providing the spectral dispersion and temporal characteristics of photoconductivity, THz spectroscopic data provide not only the values of carrier density, DC-carrier mobility and carrier diffusion length [88–91], but also the low-frequency phonon modes coupled to charge carriers [83, 84] and the binding energy of excitons [92] which are instrumental for elucidating the underlying mechanism of charge carrier transport in perovskite nanocrystals.

The dynamics of charge carriers in nanocrystal films are susceptible to the nanocrystal size due to the carrier localization effect. Motti et al. [93] measured the carrier lifetimes and mobilities of CsPbBr₃ nanocrystals with different sizes by OPTP experiments. With decreasing nanocrystal size, the carrier mobility significantly decreases and the carrier lifetime is markedly shortened. The carrier transport in nanocrystal films is mainly contributed by interdot hopping due to the coupled wavefunctions of electrons and holes between adjacent nanocrystals before recombination. Therefore, enhancing the coupling between nanocrystals by surface chemistry can lead to higher

mobility and longer lifetime. By using $\text{Pb}(\text{NO}_3)_2$ and an A-site cation halide salt treatment, Sanehira et al. [94] improved the carrier mobility and carrier lifetime of perovskite semiconductor nanocrystals. The carrier mobility increases to a value above $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in perovskite nanocrystal films which is over one-order magnitude higher than typical values of the conventional PbS and PbSe nanocrystal films, respectively. By applying oleic-acid-assisted cation exchange, the trap filling voltage in $\text{Cs}_{0.5}\text{FA}_{0.5}\text{PbI}_3$ nanocrystals in the oleic-acid-rich environment was found to be realized if compared with the nanocrystals in the oleic-acid-less environment, leading to a record power conversion efficiency of 16.6% for nanocrystal-based solar cell devices [45]. These treatments improve the charge mobility and enable the perovskite nanocrystal solar cells the most efficient in the catalog of nanocrystal solar cells.

Resonance features have also been observed in the THz spectra of perovskite nanocrystals, which were ascribed to the coupling between the charge carriers and the lattice vibration modes. For the soft lattices in perovskite semiconductors, the electron-phonon coupling may cause the deformation of lattice and result in the formation of large polaron, which was proposed to be the mechanism underlying the defect tolerance of carrier transport in perovskite

semiconductors [83, 96–98]. In the THz spectra of CsPbBr_3 nanocrystals, Cinquanta et al. [95] reported multiple resonance peaks as the fingerprints of the large polarons in CsPbBr_3 nanocrystals. By fitting the complex conductivity with Drude-Lorentz model adopting a large effective mass, the coupling phonon modes at 3 ps after photoexcitation were determined to be 27, 42 and 58 cm^{-1} (Figure 4(a)), which are assigned to the Pb–Br–Pb bending modes. These modes were reported to downshift to 24, 40 and 57 cm^{-1} at 100 ps after photoexcitation (Figure 4(b)), which were assigned to the carrier-density-dependent lattice softening due to large polaron formation. Herz and coworkers also observed a negative photoconductivity resonance in CsPbBr_3 nanocrystals at higher frequency which is also attributed to the carrier-phonon interaction [93]. In addition to the Drude response induced by charge carriers, the optical excitation in nanocrystals may also induce polarizability response in the THz spectral range [99].

2.2 Many-body effects

2.2.1 Biexcitons

In perovskite semiconductor nanocrystals, multiple excitations can occur inside single nanocrystal with increasing excitation density. The exciton-exciton interaction is manifested with Auger recombination which decays much faster than the single exciton recombination. The biexcitons, i.e., the bound complexes of two pair of electron-hole pairs, are stably formed with attractive exciton-exciton coupling. Under the assumption of Poisson distributions with excitation density, i.e., the average electron-hole pairs per nanocrystal, the light emission intensity of biexciton recombination is reported to follow a quadratic scaling with the excitation density below the saturated excitation threshold (Figure 5(a) and (b)) [62, 72, 73].

The biexciton recombination in nanocrystals is mainly caused by Auger recombination process induced by many-body interaction. The recombination rate increases with decreasing nanocrystal size due to the enhanced Coulomb interaction. The rate of biexciton Auger recombination in perovskite semiconductor nanocrystals is generally much faster than that in chalcogenides semiconductor nanocrystals. The size dependence of Auger recombination rate in perovskite nanocrystals also exhibits markedly difference. In CdSe nanocrystals, the lifetimes of biexciton are found to be nearly linearly dependent on to the nanocrystal size [71, 73]. However, in perovskite semiconductor nanocrystals, the size dependence of biexciton lifetime shows different behaviors in the weakly [62] and strongly

Figure 4: (a) Real part of the transient optical conductivity of CsPbBr_3 nanocrystals at the time delay of 3 ps (blue dots) and 100 ps (black squares), respectively. The red lines are the Drude-Lorentz fitting curves of the experimental data. (b) Real part of the Lorentzian fit of at 3 ps (red solid lines) and 100 ps (magenta dashed lines). Reproduced with permission [95]. Copyright 2019, American Physical Society.

Figure 5: (a) Pump-fluence-dependent PL dynamics of CsPbI₃ nanocrystals. Symbols A and B denote the amplitudes of the total PL signal and the single-exciton component, while $M = A - B$ denotes the amplitude of the multiexciton signal. (b) Pump-fluence-dependence of the amplitudes of single-exciton (B , black squares) and multiexciton emission components ($M = A - B$, red circles). (c) Biexciton Auger lifetimes in perovskite nanocrystals in comparison to those in CdSe and PbSe nanocrystals. (a)–(c) Reproduced with permission [62]. Copyright 2016, American Chemical Society. (d) Nanocrystal volume dependent biexciton Auger lifetimes in strongly confined perovskite nanocrystals in comparison to those in CdSe and PbSe nanocrystals. Reproduced with permission [100]. Copyright 2020, John Wiley & Sons, Ltd.

[100, 101] confined regions. In the weakly confined region, Makarov et al. [62] found a 0.5 power law of the nanocrystal volume (Figure 5(c)). In the strongly confined region, the biexciton lifetime exhibits a linear relation with the nanocrystal volume, similar to that in conventional semiconductor nanocrystals. In addition, Auger recombination rate is also dependent on the composition of perovskite nanocrystals (Figure 5(d)) [100]. For different X-site anions, the biexciton lifetime was found to be 3 times longer in CsPbI₃ than that in CsPbCl₃. While for different A-site cations, the biexciton lifetimes were similar in CsPbBr₃ and FAPbBr₃ with the same nanocrystal volume. Such a phenomenon can be ascribed to the large contribution to band-edge band structure from the X-site anions instead of the A-site cations [102].

The many-body interaction is also reflected in the ESA features of TA spectra of perovskite semiconductor nanocrystals. The ESA features can be found on both sides of the major excitonic bleaching peak (Figure 2(a)). The lower energy ESA was ascribed to the transition from single exciton to the biexciton state with attractive biexciton interaction (Figure 6(a) and (b)) [61, 62, 103, 104]. While the higher energy ESA was ascribed to the transition to high energy states activated by the existing exciton which was systematically studied by Rossi et al. (Figure 6(c) and (d)) [105]. By changing the size of nanocrystals, they found that the higher energy ESA was strengthened in strongly confined CsPbBr₃ nanocrystals, which was proposed to be related to the formation of a lattice-distorting polaron

related to the symmetry-breaking after the excitation of an exciton in nanocrystals.

Within the confined volume of single nanocrystals, the energy difference between a biexciton and two excitons is quantified as the biexciton binding energy [62]. This biexciton binding energy is defined as the energy shift for the biexciton to exciton transition relative to the exciton to the ground state transition [107]. The biexciton binding energy in perovskite semiconductor nanocrystals have been measured using the methods of PL, TA and 2DES techniques. By directly measuring PL from biexciton recombination under high fluence excitation, the binding energies of biexcitons were estimated in the range from 20 to 100 meV for CsPbBr₃ nanocrystals [101, 108, 109]. The disparity of biexciton binding energies extracted from PL measurements was ascribed to the air-exposure and high-flux irradiation [109]. Different from the PL measurements, TA can obtain the biexciton binding energy under low excitation fluence by analyzing the lower energy ESA and the excitonic PIB features. For TA measurements, the measured biexciton binding energies were reported in the range from 30 to 70 meV in CsPbI₃ nanocrystals [61, 62] and in the range from 5 to 40 meV in CsPbBr₃ nanocrystals [103, 104]. In addition to the sample diversity, the measured binding energy by TA and PL in ensemble nanocrystals may be influenced by the inhomogeneity of the sample. 2DES can disentangle the inhomogeneous broadening in the diagonal direction. Moreover, the transitions between exciton and biexciton states can be

Figure 6: (a) TA spectra of CsPbBr₃ nanocrystals at different time delays. The red and green arrows denote the PIB and the low-energy ESA features. (b) Schematic of TA evolution at early delay time. The transition energies seen by the probe pulse are modified by the exciton-exciton interaction (dashed lines). In the case of exciton-exciton attraction (shown in this sample), the energy for the transition from the exciton to biexciton states is smaller than the single-exciton transition energy. (a) and (b) Reproduced with permission [62]. Copyright 2016, American Chemical Society. (c) Schematic of light-activation of forbidden transitions in strongly confined nanocrystals. (d) Transient absorption spectra of strongly-confined CsPbBr₃ nanocrystals at 200 fs and 10 ps delay time. (c) and (d) Reproduced with permission [105]. Copyright 2018, American Chemical Society.

explicitly isolated with weak optical excitation under the proper configuration of pulse polarizations [110–113]. Huang et al. measured the binding energy of biexciton in ensemble CsPbBr₃ nanocrystals by polarization-dependent 2DES [106]. They found that the binding energies of biexcitons are in the range from 25 to 40 meV and can be explained as the size dependence within the effective mass approximation (Figure 7(a) and (b)).

2.2.2 Optical gain

For near band-edge transitions, optical gain is generated when stimulated emission can compete over the absorption with established population inversion. The threshold

of excitation density required for optical gain generation and the gain lifetime fundamentally set the potentials using perovskite nanocrystals for optical amplification and laser applications. Benefiting from strong light-matter interaction in perovskite semiconductors, optical gain can be generated over the entire visible range by exchanging the halide composition with relatively low pump threshold as characterized by fluence-dependent amplified spontaneous emission (ASE) measurements (Figure 8(c)). By coupling optical gain in optical resonators, lasers can be demonstrated using perovskite semiconductor nanocrystals with low thresholds in the range from 2 to 192 $\mu\text{J cm}^{-2}$ [23, 34, 35, 108, 114–117]. For example, Yakunin et al. [34] reported the low optical gain threshold of

Figure 7: (a) Real part of rephasing 2D spectra of CsPbBr₃ nanocrystals at 10 K with the cross-circularly polarized excitation configuration. (b) Biexciton binding energy (Δ_{xx}) as a function of nanocrystal size using the effective mass approximation. Reproduced with permission [106]. Copyright 2020, American Chemical Society.

Figure 8: (a) PL spectra measured from a solid film of CsPbBr₃ nanocrystals upon different fluence excitation and (b) the corresponding threshold behavior for the ASE intensity. (c) Spectral tunability of the ASE band by means of compositional modulation. (a)–(c) Reproduced with permission [34]. Copyright 2015, Nature Publishing Group. (d) Two-photon-pumped perovskite semiconductor nanocrystal lasers. Reproduced with permission [35]. Copyright 2016, American Chemical Society.

$\sim 5 \mu\text{J cm}^{-2}$ and demonstrated perovskite nanocrystal lasers using whispering gallery mode cavities (Figure 8(a) and (b)). Moreover, nonlinear optical absorption is also highly efficient for perovskite nanocrystals, optical gain and lasing action in perovskite semiconductor nanocrystals can be excited by multiphoton excitation process (Figure 8(d)) [35, 114, 118, 119].

The dynamics of photoexcited carriers in perovskite nanocrystals have been probed to study the physical properties underlying the optical gain generation in perovskite semiconductor nanocrystals. In principle, more than one exciton is required to generate the optical gain considering the twofold degeneracy of the band-edge transition (Figure 9(a)) [62]. As the remarkably low threshold of lasing has been achieved in neutral perovskite semiconductor nanocrystals, it has been suggested that optical gain is possibly generated in single exciton regime. Due to the overlap of spectral features of stimulated emission and ESA of different sized nanocrystals, it is challenging to fully distinguish the signals related excitons and biexcitons in the TA spectra. 2DES can tackle this issue by disentangling the signals induced by different excitation energies. Zhao et al. studied the optical gain generation by power-dependent 2DES measurements [120]. The experimental data suggest that the biexciton is required for gain generation in neutral perovskite nanocrystals (Figure 9(b)) and the gain threshold is possibly reduced to a remarkably low level benefiting

from the spectral shift caused by the mutual interaction between excitons (Figure 9(c)).

The twofold degeneracy of band-edge transition can be potentially lifted by charging the nanocrystals. For a singly charged condition, the optical gain can be achieved with population inversion established by absorption of a single photon in perovskite semiconductor nanocrystals (Figure 9(d)). In comparison with biexciton optical gain, the lifetime of trion gain is much longer, which is beneficial for low threshold optical gain. Wang et al. conducted a comparison study on the PbBr₂ treated and pristine CsPbBr₃ nanocrystals and observed the optical gain lifetime to be 620 and 330 ps (Figure 9(e)) [117]. The optical gain is achieved with an ultra-low threshold of $1.2 \mu\text{J cm}^{-2}$ in PbBr₂ treated nanocrystals (Figure 9(e) and (f)), which was ascribed to the existence of trion with extended gain lifetime.

2.3 Charge carrier dynamics under high excitation energy

2.3.1 Hot carrier relaxation

Hot carriers are generated upon excitation above the band gap. These charge carriers in higher-lying excited states will lose their excess energy and cool to the bottom of conduction band within a sub-picosecond time scale which is a major

Figure 9: (a) Mechanism for the biexciton gain in a neutral perovskite nanocrystal. (b) Absorptive 2DES spectra of CsPbBr_3 nanocrystals recorded at a population time of 5 ps under pumping fluence of $25 \mu\text{J}/\text{cm}^2$. (c) Exciton-density-dependent gain generation. The solid lines show the simulated $-\Delta\alpha/\alpha_0$ using three different models. The magenta circles indicate the signal data (2.46 and 2.39 eV) obtained in power-dependent 2DES measurements. Optical gain is achieved when $-\Delta\alpha/\alpha_0$ exceeds 1 (region inside the gray rectangle). (b) and (c) Reproduced with permission [120]. Copyright 2019, American Chemical Society. (d) Mechanism for the trion gain (positive trion as an example) in a singly charged nanocrystal with doubly degenerate band edge states. (e) Decay dynamics of the photobleach signal in untreated (black) and PbBr_2 -treated (red) CsPbBr_3 nanocrystals with a pump fluence of $2.5 \mu\text{J}/\text{cm}^2$. (f) Plots of integrated emission intensity versus pump fluence in PbBr_2 -treated CsPbBr_3 nanocrystal films. The inset shows the PL spectra for pump fluence above and below the ASE threshold. Reproduced with permission [117]. Copyright 2018, American Chemical Society.

energy loss channel in solar cells [121]. Such a relaxation process is highly non-equilibrium with multiple processes entangled on different temporal stages [122]. There are many underlying mechanisms in hot carrier relaxation process, mainly including the phonon bottleneck effect, the hot phonon bottleneck effect and Auger heating effect in perovskite semiconductors as detailed in several recent reviews [122, 123]. Here, we mainly focus on the intrinsic properties of carrier relaxation under low excitation fluence in perovskite semiconductor nanocrystals.

In bulk semiconductors, hot carriers cool to the band edge rapidly by phonon emission. This scenario may be different in nanocrystals due to the discrete excitonic states stemming from the quantum confinement effect [124]. Therefore, with the size of nanocrystals decreasing, the increased energy spacing between the discrete excitonic states may require the emission of multiple phonons, which may dramatically slow down the loss of excess energy of hot carriers, known as the phonon bottleneck effect [94, 125–128]. However, in conventional II–VI semiconductor

nanocrystals, such as CdSe nanocrystals, the existence of Auger-type electron-to-hole transfer mechanism can bypass the phonon bottleneck effect [129–131] due to the dense hole energy levels (Figure 10(a)) [130–133]. While in perovskite semiconductor nanocrystals, the effective masses of electron and hole are small and comparable [23], leading to an almost symmetric discrete energy spacing of electrons and holes, which is considered to show an intrinsic phonon bottleneck effect in perovskite nanocrystals.

The hot carrier cooling may be probed by monitoring the band edge bleach rising time, which is commonly used to study the hot carrier dynamics under low excitation fluence (under one electron-hole pair per nanocrystal) [130, 134, 135]. The hot-carrier relaxation lifetime in nanocrystals can be affected by multiple factors including the size, the surface ligands and the band structure. By monitoring the TA band edge bleaching dynamics of MAPbBr_3 bulk films and nanocrystals with different sizes, Sum et al. found that the hot carrier relaxation slowed down with the size of nanocrystals decreasing, different from the trends in

Figure 10: (a) Schematic of hot carrier cooling via the intraband Auger-type energy transfer with the electron-hole scattering (left), and intrinsic phonon bottleneck effect in perovskite nanocrystals with symmetric discrete energy levels (right). (b) Normalized bleaching dynamics probed at the band-edge for MAPbBr₃ nanocrystals and bulk film at low carrier density. (c) Size-dependent band-edge bleaching rise time and related quantum confinement energies for perovskite nanocrystals under weak quantum confinement (black square) and CdSe nanocrystals (red circle) with initial electron-hole pair per nanocrystal of ~ 0.1 . (b) and (c) Adapted and reproduced with permission [94]. Copyright 2017, Nature Publishing Group. (d) In strongly confined CsPbBr₃ nanocrystals (2.6–6.2 nm), the hot carrier relaxation time estimated by TA spectroscopy is weakly dependent on the nanocrystal size. Reproduced with permission [136]. Copyright 2019, The Royal Society of Chemistry. (e) Normalized time-resolved traces of 2DES signal probed at the band edge from CsPbI₃ nanocrystals of different sizes with excess energy of $\Delta E = 0.15$ eV. (f) Size-dependent lifetime parameters for hot carrier relaxation extracted from 2DES signals. (e) and (f) Reproduced with permission [141]. Copyright 2020, American Chemical Society.

CdSe nanocrystals (Figure 10(c)) [94]. The results suggested the existence of intrinsic phonon bottleneck effect in weakly confined MAPbBr₃ nanocrystals. In such a scenario, the high energy mode of lattice vibration is more efficient for compensating the energy spacing of the discrete excitonic states, which has been found in CsPbBr₃ nanocrystals by Zhao et al. via 2DES measurements [128]. However, Li et al. found that in strongly confined CsPbBr₃ nanocrystals [136], the hot carrier relaxation lifetimes depend very weakly on sizes of nanocrystals in 2.6–6.2 nm range (Figure 10(d)), showing a different trend compared to weakly confined MAPbBr₃ nanocrystals. Such a phenomenon, which bypassing the expected phonon bottleneck effect, was attributed to the nonadiabatic transition between excitonic states induced by surface ligands [137], due to the higher wavefunction amplitude at the surface of the strongly confined nanocrystals [138, 139].

The disparity on the size dependence of carrier cooling is possibly induced by the entanglement of the thermalization

process before establishing the quasi-equilibrium distribution during the commonly used TA measurements. The thermalization process induced by carrier-carrier interaction can occur within ~ 80 fs in bulk perovskite semiconductors [140]. Such a fast thermalization process cannot be resolved in most available TA measurements with ~ 100 fs temporal resolution. 2DES addresses this challenge with high resolution in the temporal and excitation energy domains simultaneously. By disentangling the thermalization process from the cooling process, the hot carrier dynamics of CsPbI₃ nanocrystals with different sizes have been resolved by 2DES [141]. The initial stage within ~ 20 fs contributes a large proportion of the band-edge bleach signal (Figure 10(e)), which is possibly caused by the carrier thermalization and quantum many-body interaction process in CsPbI₃ nanocrystals. The lifetime of the hot carrier cooling process increases dramatically when the size of nanocrystals decreases to the strongly confined regime, verifying the presence of a phonon bottleneck effect in CsPbI₃ nanocrystals (Figure 10(f)).

2.3.2 Carrier multiplication

When a perovskite nanocrystal absorbs a photon with energy greater than twice of the band gap, more than one electron-hole pairs may be directly excited, known as carrier multiplication. During the carrier multiplication process, the excess energy of the high-energy carrier is not dissipated by the electron-phonon interaction but transferred to the electrons in valance band and excited them to the conduction band, which can be considered as the reverse process of Auger recombination [68]. Due to the phonon bottleneck and enhanced carrier-carrier interaction, the carrier multiplication effect is significantly enhanced in nanocrystals [74, 144–147], indicating a promising potential to utilize the excess energy of high-energy carriers and improve the efficiency of solar cells by bypassing the Shockley-Queisser limit [121, 148].

Compared with conventional semiconductor nanocrystals, perovskite semiconductor nanocrystals exhibit enhanced Auger recombination as discussed above, which may also in turn enhance the carrier multiplication. The efficiency of carrier multiplication can be evaluated by comparing the ratio of the initial signal amplitude to the long-lived single exciton signal amplitude in TA temporal dynamics under different excitation energies, since the signals of multi-exciton and single exciton are at different timescales under low excitation fluence [147]. As shown in Figure 11(a), Weerd et al. [142] measured the dynamics of band-edge bleaching under different excitation energies in weakly confined CsPbI₃ nanocrystals. The consistent band-edge bleaching dynamics under pump with higher energy photon in the linear regime and lower energy photon in the nonlinear region confirmed that the fast component was generated by Auger recombination of multiexcitons.

Decreasing the size of nanocrystals is also considered to be beneficial for efficient carrier multiplication. Li et al. found that the efficiency of carrier multiplication (up to ~75%) increased with the size of nanocrystals decreasing (Figure 11(b)) [143]. The threshold of pump photon energy required by carrier multiplication in FAPbI₃ nanocrystals was found to be only 2.25 E_g which is smaller than those in conventional PbS and PbSe nanocrystals [149]. Such an efficient carrier multiplication (~90%) was also found by Cong et al. in strongly confined CsPbI₃ nanocrystals with ultrafast TA spectroscopy [150]. These findings exhibit the efficient carrier multiplication in perovskite semiconductor nanocrystals and suggest the probability toward highly efficient solar cells.

3 Spin dynamics

Spin degree of freedom is also important for the optoelectronic properties of perovskite semiconductor nanocrystals. Due to the presence of heavy atoms, the spin-orbital coupling is strong which was proposed to be responsible for long carrier lifetime in perovskite semiconductors [87]. Moreover, the spin-orbital coupling causes mixing of spin 0 and 1 excitonic states, which makes perovskite nanocrystals suitable for harvesting or sensitizing triplet exciton states of organic molecules [151–153]. In theory, it is predicted that Rashba spin-orbit effect may rearrange the order of dark and bright states [154], which has been under intensive debate. For electrically driven LED devices, the injected charges are spin random, so that it is of particularly importance to elucidate the spin-related fine levels responsible for emissive or nonemissive transitions.

Figure 11: (a) Linear vs. nonlinear regime of TA, showing the decay through Auger recombination with pumping outside the linear regime (by multiphoton absorption) and through carrier multiplication, yield the same dynamics. Reproduced with permission [142]. Copyright 2018, Nature Publishing Group. (b) Quantum yield of multiexciton generation in FAPbI₃ nanocrystals with different sizes are plotted as a function of relative pump photon energies ($h\nu/E_g$). Reproduced with permission [143]. Copyright 2018, Nature Publishing Group.

3.1 Dark state

The light-emitting properties of semiconductors are mainly determined by the recombination of band-edge excitons which could be affected by the exciton fine structure. In perovskite semiconductors, according to the density-functional-theory calculations [155–157], the band-edge excitons consist of holes in the s-like state with $1/2$ total angular momentum and electrons in the spin-orbit split-off state with $1/2$ total angle momentum. Therefore, considering the exchange interaction of electrons and holes, the combination of electrons and holes leads to a spin-allowed bright triplet state with 1 total angular momentum and a spin-forbidden dark singlet state with 0 total angular momentum.

Employing a magnetic field can split the degenerate bright triplet states owing to the Zeeman effect. By magneto-optical spectroscopy, Fu et al. [160] found that the doublet or triplet energy level induced by symmetry breaking in single CsPbBr_3 nanocrystals can be tuned by an external magnetic field at cryogenic temperatures. Such a splitting of bright triplet states can also be induced by the Rashba spin-orbit coupling effect under zero field. Isarov et al. found the nonlinear energy splitting between polarized transitions versus magnetic field strength in single CsPbBr_3 nanocrystals [161], which was ascribed to the results due to the combination of Rashba effect and Zeeman effect.

Theoretically, Becker et al. found that the Rashba spin-orbital effect can even cause the rearrangement of exciton fine structure [154], leading to a higher dark state and lower bright states (Figure 12(a)). Such an energy level alignment was considered to be responsible for the shorter PL lifetime at cryogenic-temperature than at room temperature. In contrast with the dark state lying below the bright state in conventional CdSe nanocrystals [162], the exciton fine structure was proposed to explain the more effective PL in perovskite nanocrystals.

However, it is highly controversial whether the dark state is lower than the bright states in perovskite nanocrystals. In the TRPL dynamics of a single CsPbBr_3 nanocrystal, a slow component with lifetime on the order of nanoseconds can be observed [48]. This long-lived process was also reported by Canneson et al. in the ensemble CsPbBr_3 nanocrystals [163]. They found that the long-lived process can be controlled by magnetic field and temperature, indicating the contribution of the dark state to this long-lived process. Chen et al. measured the temperature-dependent TRPL in ensemble nanocrystals (Figure 12(b)) [158] and demonstrated that the enhanced long-lived process at low temperatures was caused by the reduction of

thermal excitation via phonons from lower dark state to higher bright state (Figure 12(b)). By changing the composition of cations and halide anions, they confirmed that this mechanism is ubiquitous in lead halide perovskite nanocrystals, and found that the energy splitting between bright and dark states can be adjusted by different cations and halide anions. The possible polymorphs of perovskite semiconductor nanocrystals have been considered to explain the disparity between the experimental data and theoretical model [164]. Recently, Tarmart et al. [159] used an external magnetic field in a single FAPbBr_3 nanocrystal to brighten the dark state (Figure 12(c)). Different from the model proposed by Becker et al. [154], the lower lying dark state was directly observed, which indicates that the electron-hole exchange interaction dominates the energy splitting of the bright and dark states in nanocrystal. Recent theoretical work by Sercel et al. has proposed a possible explanation on the controversy [165]. They found that the distribution of bright and dark states is determined by the competition of electron-hole exchange interaction and Rashba effect which will be affected by the quantum confinement effect. According to their theoretical model, the Rashba effect will be more prominent under weak quantum confinement effect. It is worth noting that the energy gaps between nonemissive and emissive states can be compensated by thermal activation energy at room temperature, which is unlikely to be a factor limiting the LED performance.

3.2 Spin relaxation

Spin relaxation process in perovskite semiconductor nanocrystals has also attracted much attention. In general, three processes have been regarded as the major pathways for spin relaxation in semiconductors, namely Elliott-Yafet mechanism, the Dyakonov-Perel mechanism and the Bir-Aronov-Pikus mechanism [168]. In the Elliott-Yafet mechanism, the spin relaxation is dominated by the scattering with phonons and impurities [166, 169–172]. The Dyakonov-Perel mechanism is related to the spin-orbit splitting probably induced by Rashba and Dresselhaus effects in noncentrosymmetric semiconductors [173–176]. The Bir-Aronov-Pikus mechanism is caused by the exchange interaction between the electrons in the conduction band and holes in the valence band [177]. Understanding the spin relaxation mechanism in semiconductors is instrumental for designing systems with long spin relaxation times to realize spintronic applications. The spin polarization of electrons can be introduced by circularly

Figure 12: (a) Theoretically predicted fine level structures of band-edge exciton considering the electron-hole exchange interaction and the Rashba effect in perovskite nanocrystals. Reproduced with permission [154]. Copyright 2018, Nature Publishing Group. (b) TRPL curves of CsPbBr₃ nanocrystals recorded at different temperatures. The inset depicts a three-level model with the ground state (G), bright state (B) and dark state (D). Reproduced with permission [158]. Copyright 2018, American Chemical Society. (c) The one-, two-, and three-peaked PL spectra measured from three different FAPbBr₃ nanocrystals at 4 K in zero magnetic field (upper) and the corresponding four-peaked PL spectra measured at 4 K in magnetic field as marked (lower), respectively, revealing the lowest-energy singlet dark-exciton peak. Reproduced with permission [159]. Copyright 2019, Nature Publishing Group.

polarized light excitation, and the spin relaxation dynamics can be obtained by detecting the population of spin states at different delay times (Figure 13(a)), as established in previous studies of crystal [178], bulk [175, 179] and quantum well [180] of perovskite semiconductors.

Due to the enhanced electron-hole exchange interaction and possible existence of Rashba effect, the spin relaxation mechanism is complicated in perovskite semiconductor nanocrystals. Recently, Strohmair et al. [166] measured the spin relaxation dynamics in CsPbI₃ nanocrystals via

temperature-dependent polarization-controlled TA at different temperatures. They found a more than 1 order of magnitude slower spin relaxation at cryogenic temperature (32 ps) than at room temperature (3 ps), suggesting that carrier-phonon scattering plays a significant role in spin relaxation in CsPbI₃ nanocrystals corresponding to the Elliott-Yafet mechanism (Figure 13(b)). Such a spin relaxation lifetime at room temperature (~3 ps) in CsPbI₃ nanocrystals is much longer in its bulk counterparts (~1.3 ps) [179]. In this scenario, decreasing the size of nanocrystals was

Figure 13: (a) Schematic of optical transitions between valence and conduction band states induced by circularly polarized light. (b) Normalized polarization-dependent TA traces recorded from the CsPbI₃ nanocrystals at 50 and 250 K, respectively. (a) and (b) Adapted and reproduced with permission [166]. Copyright 2020, American Chemical Society. (c) Size dependent spin-relaxation rate for CsPbI₃ (red) and CsPbBr₃ (green) nanocrystals. The red and green dashed lines are values for bulk counterparts, respectively. Reproduced with permission [167]. Copyright 2020, American Chemical Society.

supposed to further retard the spin relaxation lifetime. However, Li et al. [167] found that the spin relaxation rates increase as the sizes of nanocrystals decrease in either CsPbI₃ or CsPbBr₃ nanocrystals (Figure 13(c)). Moreover, the spin relaxation lifetime in CsPbBr₃ nanocrystals was found to be shorter than its bulk counterparts, different from that in CsPbI₃, which was attributed to the different mechanism in CsPbBr₃ (Dyakonov-Perel mechanism) and CsPbI₃ (Elliott-Yafet mechanism). These findings suggest that the spin relaxation lifetime in perovskite nanocrystals might also be affected by other factors originating from quantum confinement effect and need to be further studied.

Perovskite semiconductor nanocrystals exhibit polymorphs with different shapes even in a same bunch of nanocrystal samples. Due to the spin-orbit coupling, the inversion symmetry breaking in the non-cubic phases may cause different energy alignment of excited states with different spin characters. These effects may complicate the dynamics of excited states and spin depolarization. Tao et al. [181] studied the polaronic effect on the spin relaxation dynamics in two-dimensional CsPbBr₃ nanoplates. They found that as the temperature decreases, the spin relaxation rate increased, which is ascribed to the weakened coupling of electron-lattice vibration suppressing the formation of polarons. Moreover, the spin relaxation rate shows marginally linear dependent on excitation density with a slope ~ 60 times smaller than that in two-dimensional transition metal dichalcogenides, which is ascribed to the screened exciton-exciton interaction. The anomalous exciton spin relaxation dynamics suggests the role of polaronic screening character in two-dimensional perovskite nanoplates, showing the opportunity to design low-dimensional quantum confined systems for spintronic applications.

4 Coherent exciton dynamics

Due to quantum confinement, semiconductor nanocrystals have been regarded as “artificial atoms” with discrete low-lying energy levels. The excitonic transition in a single nanocrystal has been proposed as a quantum two-level system, i.e., a solid-state quantum qubit, for quantum information applications. The main parameter that characterizes quantum coherence of a two-level system is the dephasing time, i.e., the intrinsic linewidth [187]. Single-nanocrystal spectroscopic experiments, as well as time-domain four-wave mixing and 2DES measurements, have been conducted to characterize these essential parameters based on isolating the individual nanocrystal or the identical nanocrystals from the ensemble.

In CdSe semiconductor nanocrystals, the PL linewidths of single nanocrystals suffered from the blinking and spectral diffusion effects, which were ascribed to the trion Auger recombination [188] and local electric field induced by surface-trapped charge carriers [189], respectively. In perovskite nanocrystals, these effects are significantly suppressed especially under low-fluence excitations, leading to excellent single-photon emission properties with narrow linewidths [48, 75]. Hu et al. [75] studied the PL of single CsPbI₃ nanocrystals, they found that the PL linewidths can be less than ~ 200 μeV as limited by the resolution of spectrometers at cryogenic temperature. Additionally, the suppressed blinking and spectral diffusion effects in single perovskite nanocrystals provides the opportunity to distinguish the PL from the split of bright triplet states induced by reduced structural symmetry [160, 190]. The experimental evidence about the excitonic triplet fine structure in perovskite nanocrystals

Figure 14: (a) PL spectrum measured from a single $\text{CsPb}(\text{Cl}/\text{Br})_3$ nanocrystal with three emission peaks. Reproduced with permission [182]. Copyright 2016, American Chemical Society. (b) Time-dependent PL spectra from a single CsPbI_3 nanocrystal excited at $N \sim 1.5$ with different emission species marked on the top by XX^- , XX , X^{2-} , X^- and X , respectively. Reproduced with permission [183]. Copyright 2017, American Physical Society. (c) For a single CsPbBr_3 nanocrystal with $\Omega_1 = 0.109 \text{ meV}$, the dephasing time of exciton fine structure of $T_2 = 78 \text{ ps}$ can be fitted from the photon-correlation Fourier spectroscopy data, corresponding to a PL linewidth of $\Gamma = 17 \mu\text{eV}$ estimated from the Fourier-transformed spectral correlation (inset). Reproduced with permission [184]. Copyright 2019, American Association for the Advancement of Science. (d) Quantum interference measurement of a single CsPbI_3 nanocrystal. Inset exhibited the PL intensity measured at $\tau_c = 12 \text{ ps}$ as a function of τ_f showing an oscillating behavior due to quantum interference between the wavefunctions of two excitons. Reproduced with permission [185]. Copyright 2019, American Chemical Society. (e) Four-wave mixing field amplitude as a function of the time delay τ_{12} between the first and the second pulse in the temperature 5–50 K for fixed $\tau_{23} = 1 \text{ ps}$. Inset: Schematic of the three-beam pulse sequence and the resulting photon echo. Reproduced with permission [186]. Copyright 2018, American Chemical Society.

was captured by measuring PL emission from single $\text{CsPb}(\text{Cl}/\text{Br})_3$ nanocrystals with three peaks at cryogenic temperatures (Figure 14(a)) [182]. Alternatively, doublet peaks were also frequently captured in PL spectra from single CsPbI_3 nanocrystals [183], which were ascribed to the different symmetry of the different phases in nanocrystals. The excitonic level in the cubic phase at higher temperature splits into a doublet states and a non-degenerate state in the tetragonal phase, but three non-degenerate states in the orthogonal phase [190–193]. Yin et al. [183] also found that the doublet emission from neutral single exciton can switch into a single peak of singly charged exciton under an intermediate excitation fluence. The doublets from neutral biexciton, charged biexciton and doubly charged single exciton were additionally observed under high-fluence excitation indicating abundant bright exciton fine structure in perovskite nanocrystals (Figure 14(b)).

The spectral resolution limit can be addressed by measuring the temporal correlation of single photon emission employing interferometry-based approaches. Using photon-correlation Fourier spectroscopy, Utzat et al. studied

the coherent exciton dephasing in the exciton fine structure of single CsPbBr_3 nanocrystals bypassing the influence of spectral diffusion. The typical dephasing time is estimated to be $\sim 78 \text{ ps}$ for a specific single CsPbBr_3 nanocrystal (Figure 14(c)), [184] which is close to the PL decay lifetime. Without correcting the spectral diffusion, Lv et al. directly used the Michelson-type interferometry and characterize the dephasing time of excitons to be $\sim 10 \text{ ps}$ (Figure 14(d)) [185]. The long dephasing time implies the promising potential using perovskite nanocrystals to produce indistinguishable single photons.

The coherent exciton dynamics can also be measured in ensemble nanocrystals with time-resolved spectroscopy. Using time-domain four-wave mixing technique [194], Becker et al. [186]. Reported the dephasing time of excitons $\sim 24.5 \text{ ps}$ at 5 K in the ensemble CsPbBr_2Cl nanocrystals (Figure 14(e)). 2DES can acquire the linewidths and the temporal coherent dynamics between different states simultaneously [195]. Liu et al. [196] studied the coherent properties of ensemble CsPbI_3 nanocrystals through polarization-controlled 2DES. The exciton fine structure was directly measured by cross-linear 2DES. The dephasing time between the exciton fine structure

extracted from the zero-quantum spectra was 1.36 ps at 20 K, and the dephasing time of the triplet exciton was also measured up to ~5 ps by extracting the homogeneous linewidths in cross-linear and colinear one-quantum spectra. By employing the cross-circular 2DES, Huang et al. [106] reported uncorrelated linewidth broadening for exciton and biexciton-related transitions.

Interestingly, the electronic coherence may be established among coupled individuals of perovskite semiconductor nanocrystals at the ensemble level manifesting with superfluorescence emission. When the individual emitters of different nanocrystals interact coherently via a fluorescence radiation field, the coupled dipoles exhibit coherent emission with significant increase in radiative emission rate. The cooperative superfluorescence occurs on a time scale shorter than the lifetime of random spontaneous emission [197, 198]. In perovskite nanocrystals, such a phenomenon was demonstrated by Raino et al. [197]. In a self-assembled CsPbBr₃ superlattice via bunched photon emission, redshifted emission, shortened lifetime and Burnham-Chiao ringing in the time domain at high excitation density.

5 Summary

In this review, we summarize the recent progresses on the photoexcited carrier dynamics in perovskite semiconductor nanocrystals studied by a variety of spectroscopic methods. For optoelectronic applications, perovskite nanocrystals have shown efficient radiative recombination and moderate charge mobility which enables high performances in the light-emitting and solar conversion devices. The long-lived hot carriers and efficient carrier multiplication suggest the promising potential using perovskite nanocrystals for new conceptual devices beyond the detailed balance limit. The carrier dynamics upon high density excitation, especially these biexciton and trion-related features, are instrumental for optical gain generation in perovskite nanocrystals. The interplay between the electron-hole exchange interaction and the spin-orbital interaction results in exciton fine structures of perovskite nanocrystals, providing an emergent platform to demonstrate solid-state quantum information devices.

The novel type of semiconductor nanostructures is also facing some challenging problems such as the surface, the chemical stability and the polymorph that need to be solved in the future [57, 199]. The sample diversity may be also the reason underlying some controversial dynamics reported so far. In working devices, the interface also plays an important role so that it is important to capture the information about the dynamics of the interfacial energy and charge transfer in

the future. In addition to the cubic shaped nanocrystals summarized here, the carrier dynamics are also susceptible to the shape and dimensionality of perovskite nanocrystals, which offers new opportunity for material design toward optoelectronic applications.

6 Final note

By no means does this paper present a comprehensive review of perovskite nanocrystals with ultrafast optical spectroscopies. We, and as such the authors, have not attempted to review the enormous body of published results. Instead, the authors have focused on a few selected results to illustrate the concepts, methodologies and physics behind described phenomena. We apologize for possible omissions.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work is supported by the National Key R&D Program of China (Grant Nos. 2017YFA0303700 and 2018YFA0209101), the National Science Foundation of China (Grant Nos. 21922302, 21873047, 11904168, 91833305, 91850105), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the Fundamental Research Funds for the Central University.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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