Highly Enhanced Exciton Recombination Rate by Strong Electron–Phonon Coupling in Single ZnTe Nanobelt

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Supporting Information

ABSTRACT: Electron–phonon coupling plays a key role in a variety of elemental excitations and their interactions in semiconductor nanostructures. Here we demonstrate that the relaxation rate of free excitons in a single ZnTe nanobelt (NB) is considerably enhanced via a nonthermalized hot-exciton emission process as a result of an ultrastrong electron–phonon coupling. Using time-resolved photoluminescence (PL) spectroscopy and resonant Raman spectroscopy (RRS), we present a comprehensive study on the identification and the dynamics of free/bound exciton recombination and the electron–phonon interactions in crystalline ZnTe NBs. Up to tenth-order longitudinal optical (LO) phonons are observed in Raman spectroscopy, indicating an ultrastrong electron–phonon coupling strength. Temperature-dependent PL and RRS spectra suggest that electron–phonon coupling is mainly contributed from Light hole (LH) free excitons. With the presence of hot-exciton emission, two time constants (∼80 and ∼18 ps) are found in photoluminescence decay curves, which are much faster than those in many typical semiconductor nanostructures. Finally we prove that under high excitation power amplified spontaneous emission (ASE) originating from the electron–hole plasma occurs, thereby opening another radiative decay channel with an ultrashort lifetime of few picoseconds.

KEYWORDS: ZnTe nanobelts, exciton dynamics, electron–phonon coupling, photoluminescence, resonant Raman spectroscopy

The understanding and control of the exciton relaxation properties in semiconductor nanostructures is of fundamental scientific interest because of their direct relevance to the practical applications in linear and nonlinear optoelectronic and photovoltaic devices.1−6 The exciton relaxation process and associated relaxation dynamics are highly dependent on the band structure, the types of phonons involved, and their respective coupling strength to electrons or excitons.7−9 In polar semiconductors (such as ZnO, CdS, GaAs, etc.), free excitons are strongly coupled to LO phonons via Fröhlich interaction, which can lead to a much faster carrier radiative rate than the nonpolar semiconductors.10−12 During a typical intravalley relaxation process, the photoexcited carriers lose their excess energy to crystal lattice by emission of either longitudinal optical (LO) or acoustic phonons, relaxing to the $k \sim 0$ momentum states.7 Since the typical relaxation time for LO and acoustic phonons are on the scale of ∼100 fs to ∼100 ps, respectively, which is much shorter than the exciton recombination time scale (∼1 ns), the emission of a nonequilibrium elementary excitation produces “hot excitons” that have been observed in these polar semiconductors.13−16

The “hot-exciton” emission considerably enhances the radiative rate of the carriers. However, in most of as-reported II–VI semiconductors such as ZnO and CdS, the exciton decay path is still dominated by thermal-equilibrium recombination processes; thus, the decrease of exciton decay rate by electron–phonon coupling is limited, and the exciton lifetime is on the scale of several hundreds of picoseconds or even longer. Recently, through coating a layer of SiO2/Ag shell to CdS nanowire, Cho et al. succeeded in tuning the recombination process in CdS nanowires from one at thermal-equilibrium to a hot-exciton recombination process through the plasmon-enhanced exciton–phonon coupling effect, resulting in a decrease of the exciton lifetime by a factor of ∼1000.3 Herein we demonstrate a very strong electron–phonon coupling in ZnTe NB with which the radiative rate of a single bare ZnTe NBs is significantly enhanced (∼18 ps), involving the so-called “hot-exciton” emission.

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Zinc telluride (ZnTe), a direct gap semiconductor with a bandgap of 2.26 eV at room temperature, is one of the most promising materials for optoelectronic devices in the pure green region.17 It has many unique applications in the domains of terahertz generation and detection, radiation detector, acoustooptic devices, and photorefractive substrates in optical data processing as well as in other telluride compounds.17–20 A clear understanding of its excitonic properties (generation, decay, transport, etc.) is particularly important for improving the performance of those optoelectronic devices. However, unlike other II–VI semiconductor nanostructures such as ZnO, CdS, and CdTe, whose exciton properties have been extensively studied, the excitonic dynamics of ZnTe nanostructures are rarely explored, especially in the time domain.5,21,22 Until now, many experimental and theoretical efforts have been devoted to the growth and steady-state PL characterizations of ZnTe epilayers and nanostructures.17,18,23–27 In epilayer structures, the lattice mismatch and difference in thermal expansion coefficient with the substrate induces a source of strain, structural defects, and element doping states, giving rise to the difficult and controversial assignment of the emission.17,28,29 The crystal quality of ZnTe fabricated so far in nanowire and nanocrystal forms are also not as good as that of other II–VI semiconductors.18,24,27 ZnTe in nanobelt (NB) form may circumvent this problem effectively.19 Our research is motivated to obtain a clear understanding of mechanism and nature of the exciton recombination dynamics of ZnTe materials following photoexcitation. In particular, the mechanism of electron–phonon coupling and its reduced nonequilibrium hot-exciton emission are explored in energy and time domains.

In this paper, we investigate the exciton dynamics in the ZnTe NB between the regions of spontaneous and amplified spontaneous emission (ASE) using steady-state and time-resolved photoluminescence spectroscopy (TRPL) and resonant Raman spectroscopy (RRS). The origins of the excitons are elucidated, and the emission peaks are assigned with the support of first-principles calculations. We find that LO phonons are strongly coupled to the LH free excitons, leading to the emission of the tenth-order LO phonons (10th-LO). The decay rate of the excitons is highly enhanced with the occurrence of the hot-exciton process.

Figure 1a,b displays typical scanning electron microscopy (SEM, JEOl 7001F) and low-magnification transmission electron microscopy (TEM, JEOl JSM-7001F) images of the as-grown NBs (see methods in Supporting Information). The thickness of the nanobelts is from 40 to 300 nm, and the width is on the scale of 100 nm–10 μm. The high-resolution TEM (HRTEM) image displayed in Figure 1c shows that the ZnTe NB has a single zincblende crystalline structure. The clear and sharp diffraction spots in the power spectra obtained from HRTEM images (Figure 1d) suggest the good quality of the ZnTe NB. The growth direction of the ZnTe NB is [111].21 The observed lattice fringes on HRTEM images correspond to 0.352 and 0.305 nm for (111) and (002) interplanar distances, respectively, matching with a calculated cell parameter of 0.61 nm (a = b = c).19 Raman scattering spectroscopy is a powerful technique to study the phonons in the semiconductor nanostructures. The peak position and line shape parameters carry important information concerning the crystalline quality, structural defects, and novel phonon states associated with size or anisotropic shape.20,30,31 In particular, resonant Raman scattering (RRS) is effective to probe the electron–phonon interactions and electronic structures.12,13,32–34 The overtones/fundamental Raman peak intensity ratio in RRS spectra can be used to evaluate the electron–phonon coupling strength.12,32–34 In ZnTe nanorods, we have recently observed a strong electron–phonon coupling with a Huang–Rhys factor ~3 using RRS.32 Nevertheless, a few more key questions remain to be addressed. For instance, how does the exciton contribute to the LO phonon scattering cross section? What is the outcome of the exciton dynamics due to such strong electron–phonon coupling strength?

When the NB is excited by a 473 nm laser, only one emission band is observed with a peak at 548.4 nm (ca. 2.26 eV), as shown in Figure 2a.35 As the NBs are excited by a 514 nm laser, in addition to the PL emissions, several narrow peaks are observed (Figure 2b).35 As the NBs are excited by a 514 nm laser, in addition to the PL emissions, several narrow peaks are observed (Figure 2b).35

Figure 2. (a–c) Steady-state PL and Raman spectra of a single ZnTe nanobelt at room temperature. The excitation wavelength is 473 nm (a), 514 nm (b) and 532 nm (c), respectively. (d) Schematic diagram of cascade model.
observed corresponding to phonon emissions of ZnTe. Three peaks located at 110, 120, and 145 cm\(^{-1}\) are assigned to \(E_{\text{LO}}\), \(A_{\text{1}}\), and \(E_{\text{LO}}/E_{\text{TO}}\) modes of the crystalline Te phase as reported in ZnTe NRs.\(^{32}\) Seven other peaks located at 205, 410, 615, 820, 1025, 1230, and 1435 cm\(^{-1}\), nearly the multiple of \(\omega_{\text{LO}} = 205\) cm\(^{-1}\), are the corresponding \(n\)-th-order (\(n = 1, 2, 3, 4, 5, 6, 7\)) LO phonon emission peaks, respectively. Compared to the appearance of high-order LO peaks, Raman peaks of TO phonons are not resolved, suggesting the dominant Fröhlich interaction in ZnTe NBs.\(^{32}\)

By introducing the idea of the “cascade relaxation model”, in which hot excitons serve as intermediate states, Gross et al. and Klein et al. explained the multiphonon Raman spectroscopy in II–VI semiconductor compounds.\(^{36,37}\) This process can be qualitatively described as follows (indicated by red curves in Figure 2d): a primary photon with energy of \(\hbar\omega_0\) creates a hot exciton together with the emission of one LO phonon, and then the exciton is scattered multiple times by LO phonons into states separated by \(\hbar\omega_{\text{LO}}\). Finally, there is an indirect annihilation of the exciton with one more LO phonon and a secondary photon with energy \(\hbar\omega_0 - \hbar\omega_{\text{LO}}\).\(^{37}\) The RRS process expressed above is very similar to that of real-state hot-exciton emission. It is argued that the two processes originate from different physical phenomena: in the hot-exciton emission process the participation of real exciton states is required but not in multiphonon resonant scattering.\(^{13,15}\) However, so far it is still hard to distinguish them in the optical spectrum.\(^{13}\) The hot-exciton emission also consists of a series of narrow lines shifted by integer numbers of LO phonons from the excitation energy.\(^{13}\) Leite et al. ascribed the LO emissions of CdS crystal to RRS; however, Pergarov et al. suggested that only part of the emissions were associated with hot-exciton emissions.\(^{10,13}\) Martin et al. suggested that the inelastic scattering of light in CdS crystals occurs as a cascade process containing aspects of hot-exciton luminescence and Raman scattering.\(^{36}\) In some cases such as exciton–polariton states involved emissions, it is meaningless to distinguish the two processes.\(^{13}\) In ZnTe NBs, it is more likely that RRS and hot-exciton emission process occur simultaneously. First, the opening up of fast hot-exciton emission channel will accelerate the decay of exciton in excited states extensively.\(^{3,13,14,37}\) Experimentally, we have observed significant shortening of carrier radiative rate which is demonstrated not due to surface states (to be discussed later). Additionally, only two LO emission lines are observed below the center of PL emission peaks in Raman spectra taken at both 532 and 514 nm excitation cases, similar to that was observed in CdS crystals.\(^{10}\)

Lastly, the intensity differences of the high-order LO overtones are not as large as those obtained from the multiphonon Raman scattering process.\(^{13}\) When the NB is excited by 532 nm excitation, the 3rd-LO intensity is almost the same with 2nd-LO, which is in good agreement with hot-exciton emissions (Figure 2c).

The exciton/carrier decay dynamics is highly dependent on the type, population, and symmetry of excitons.\(^{9}\) To obtain a clear understanding of the nature and origin of excitons in ZnTe NBs, we have carried out low-temperature steady-state PL spectroscopy. Figure 3a,b shows the PL spectra of a single ZnTe NB under the excitation of a 473 nm laser. As the temperature decreases, the PL emission peak blue-shifts and the peak width becomes narrower and narrower. When the temperature is around 90 K, the PL emission band splits into several peaks, with an additional new band around 2.30 eV, which we assign to donor-acceptor pair emission (to be discussed in detail later). As the temperature decreases to 30 K or even lower, more spectral details and finer emission features are resolved. The PL emission at 13 K (Figure 3a) is dominated by near-band edge emission around 525 nm (ca. 2.37 eV). In some literatures, strong Y emission around 600–700 nm was observed due to strains or elemental doping.\(^{38,39}\) In the as-grown NBs, no such similar emission was observed in this region (data not shown here), justifying the absence of strain or extrinsic doping. To accurately determine the values of position and full width at half-maximum (fwhm) of each peak, we fit the experimental data (open blue circles) with least-squares fitting results based on the Varshni equation.\(^{13}\)

The degeneracy of the conduction bands and valence bands are 2-fold (\(\Gamma_{5h}\)) and 4-fold (\(\Gamma_{7h}\)), respectively, in zinc-blende semiconductors.\(^{40}\) Because of a large spin–orbit splitting, only excitons with the hole in the topmost (\(\Gamma_7\)) valence band are observed. The ground state of this exciton splits to three types of exciton states—\(\Gamma_p\), \(\Gamma_m\), and \(\Gamma_s\)—while only the \(\Gamma_7\) exciton state is dipole-allowed.\(^{40}\) Because of the strains in the crystal, the 4-fold of valence band is reduced, leading to the splitting of \(\Gamma_7\) into heavy hole (HH) and light hole (LH) free excitons, respectively.\(^{40}\) Previous reflectance and PL spectroscopy have shown that the ground-state (1S) heavy hole free exciton (\(X_{\text{HH}}^{1\text{S}}\)) and light hole free exciton (\(X_{\text{LH}}^{1\text{S}}\)) of ZnTe epi-layer are located at 2.379 and 2.375 eV at 2 K, respectively.\(^{38,39}\) In our PL spectrum at 13 K, the two most noticeable peaks are located at 2.377 and 2.372 eV; therefore, we assign them to be free
exciton \(X_{\text{HH}}\) and \(X_{\text{LH}}\), respectively. The assignment can be justified based upon two reasons. First, no luminescence lines are found above the two peaks as the temperature increases from 13 to 300 K. Previous studies have reported bound emission peaks around 2.375 eV due to neutral acceptors caused by extrinsic elemental doping (Li, Ag, Cu). However, in those studies, strong free exciton emissions were observed in the high-energy part of the bound exciton emission. With increasing of temperature, the bound exciton emission decreases rapidly because of the ionization effect and the free exciton emission thus becomes dominant. The temperature-dependent emission position \(E(T)\) of the two peaks (Figure 3c) can be well fitted with Varshni function \(E(T) = E_0 + T\alpha(\beta + T)\), where \(\alpha = 0.6\ \text{meV/K}\) and \(\beta = 160\ \text{K}\) in good agreement with previous studies, underpinning the validity of the assignment.\(^{41}\)

The emission peak near 2.368 eV is weaker than \(X_{\text{HH}}\) and \(X_{\text{LH}}\). This emission feature has been reported by many other groups and assigned to \(X_n\) referring to excitons bound to a neutral shallow acceptor. The source of this peak is still controversial. Extrinsic element diffusion from substrate, including P, As, Li, Ag, and Cu, has been reported to introduce shallow acceptors, giving rise to the emission peak ∼2.368 eV.\(^{17,28,42}\) Unlike its epilayer counterpart, which has a lot of free band at 2.32 eV, the emission peak near 2.368 eV is due to neutral acceptors.\(^{23,28,39}\)

Figure 4a shows the RRS spectra of single ZnTe NB taken at different temperatures. The red arrows indicate the \(X_{\text{LH}}\) position at each temperature. (b) Integrated intensity ratio of LO, LO + TO, and 2LO modes as a function of temperature.

\[ \text{temperature from 13 to 240 K. Since the LO overtones are much stronger than the other Raman peaks such as SO and TO, the Raman intensity has been logarithmically scaled such that other Raman peaks and fine features can be resolved clearly. The observation of SO phonons in Raman scattering is due to the breaking of translational symmetry in nanostructures, which has been discussed in detail in a wide range of nanowires and nanobelts.30,32,46 With increasing temperature, more and more LO overtones are resolved. The intensity of those Raman peaks located near or at \(X_{\text{LH}}\) is stronger than that of the other peaks, while the red arrows in Figure 4a indicate the position of \(X_{\text{LH}}\). The trends can be seen clearly from the integrated Raman intensity as a function of temperature (Figure 4b). In the temperature region of 13−90 K, the exciton line width \(\Gamma\) is almost the same (also seen in Figure S2, Supporting Information); thus, the Raman intensity is mainly determined by the exciton energy \(E_{\text{ex}}\). The intensity profile of each LO, TO + LO, and 2LO peak show a single maximum, where \(E_{\text{ex}} = h\omega_{\text{LO}} - h\omega_0\), suggesting that the \(X_{\text{LH}}\) is enhanced dramatically as the \(X_{\text{LH}}\) energy is in resonance with 9th-LO phonons at 40 K, as shown in Figure 3d. A similar feature was found in CdS nanowire with Ag serving as shell by Cho et al. and ascribed to the dominant of hot-exciton emission generation.\(^{3}\)

Next we discuss the temperature-dependent resonant Raman spectroscopy. We would like to address which exciton is involved in the strong electron–phonon coupling in ZnTe nanostructures. By varying the temperature, the exciton emission position is tuned in resonance to the incidence and scattering radiation energy such that the intensity of each Raman peak can be accurately probed. The Raman scattering cross section for an nth Stokes LO phonon process is given by

\[ \text{R}^{(n)}(\omega) = \mu_n^2 \sum_{m=0}^{\infty} \left( \frac{\langle n|m\rangle \langle m|i\rangle}{E_{\text{ex}} + n\hbar\omega_{\text{LO}} - \hbar\omega_0 + \hbar\omega_i} \right)^2 \]

where \(\mu\) is the electronic transition dipole moment and \(\hbar\omega_i\) and \(\hbar\omega_i\) denote the initial states and the intermediate vibration level in the excited state, respectively. The resonant Raman scattering occurs when the denominator becomes zero. Thus, the LO overtone intensity will be sensitive to the exciton energy \(E_{\text{ex}}\) and its line width \(\Gamma\).
The energy of the exciton in strong resonance with LO + TO ($E_a = \hbar\omega_b - \hbar\omega_{1LO+TO}$) is higher than that of 2LO ($E_a = \hbar\omega_b - \hbar\omega_{2LO}$). The exciton energy decreases with the increasing of temperature; thus, the highest Raman intensity of LO + TO is obtained at a lower temperature (30 K) than that of 2LO (60 K).

A hallmark of the hot-exciton process is its fast decay rate. The typical recombination time constant of general nonthermalized exciton recombination is around ~1 ns. In the hot-exciton emission process, the excess energy of the exciton is dissipated mainly by the emission of LO phonons, leading to a recombination time scale of tens of picoseconds. Transient PL spectroscopy, with varied pump power density, has been conducted to probe the exciton recombination dynamics of ZnTe NBs. As Figure 5a,b shows, the PL decay curve can be well fitted by a double-exponential decay equation as follows

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$$

where $\tau_1$ and $\tau_2$ are time constants for two decay paths and $I_1$ and $I_2$ are the corresponding amplitude of PL intensity. When the pumping fluence is below 5 $\mu$J/cm$^2$, $\tau_1$ and $\tau_2$ are 80 and 18 ps; the respective amplitudes $I_1$ and $I_2$ are 0.18 and 0.82. The two time constants, especially $\tau_2$, are much smaller than PL emission lifetime reported in many other semiconductors. In nanostructures, the PL lifetime could be reduced by surface states related nonradiative process, with a reported decay time still on the order of ~100 ps. In order to rule out the influence of surface state, a 200 nm thick PMMA layer was spin-coated onto the ZnTe NBs sample substrate. The transient PL spectrum (Figure 5b, red curve) is almost the same as that of bare ZnTe NB, suggesting that the two short time constants are intrinsic properties. The free exciton lifetime of ZnTe was considered to be <100 ps; however, the exact value was not obtained in that experiment due to their instrument limit. Here $\tau_1$ is measured to be ~80 ps, which is in good agreement with above study; thus, we attribute it to the free exciton lifetime. The faster decay path, with a time constant $\tau_2 \sim 18$ ps, has much higher amplitude (0.82) than free exciton decay path (0.18). Thus, it is difficult to assign the fast decay path to surface related nonradiative decay as that was commonly done in other nanostructures. Additionally, the amplitude of surface states related nonradiative decay path would decrease significantly under high power density since the surface states are fully occupied. However, here the amplitude of the fast decay path shows no noticeable decrease as the increasing of pumping fluence. The lifetime of the fast decay path (18 ps) is close to that was obtained in the CdS/SiO$_2$/Ag system (7 ps). It is therefore reasonable to attribute the fast decay path to hot-exciton emission.

As the pumping fluence approaches 30 $\mu$J/cm$^2$, the overall emission decay becomes much faster (Figure 5c–e) and an additional shorter lifetime ($\tau_3 \sim 5$ ps) appears, due to the opening up of a multiexciton decay channel by amplified spontaneous emission (ASE). The occurrence of ASE can be clearly seen in the corresponding steady-state PL spectra in Figure 5f. The emission intensity increases linearly as the pump fluence is increased from 5 to 30 $\mu$J/cm$^2$. When the pumping fluence is 35 $\mu$J/cm$^2$, an intensely sharp peak located at 552 nm appears with a fwhm of ~3 nm. The intensity of PL emission versus the pump fluence, plotted in the inset of Figure 5g, suggests an ASE threshold of ~32 $\mu$J/cm$^2$.

The mechanism of ASE for II–VI semiconductor such as ZnO and CdS is exciton–exciton scattering in low temperature ($T \sim 70$ K). At higher temperature, ASE is contributed by exciton–electron scattering. As the concentration of exciton or carrier is larger than the critical Mott transition density, the Coulomb field between the electrons and holes gets screened; excitons will condense and form an electron–hole plasma with a smaller energy than that of excitons. In II–VI semiconductors, Mott density can be expressed as $n_m = (k_bT/16\pi\hbar^2a_0^3)$, where $k_b$ is the Boltzmann constant, $E_b$ is the binding energy of exciton, and $a_0$ is the Bohr radius. Substituting $E_b = 13$ meV and $a_0 = 5.2$ nm, the Mott density of ZnTe at room temperature (300 K) is $3.4 \times 10^{17}$ cm$^{-3}$. 

**Figure 5.** Power-dependent time-resolved PL spectroscopy of single ZnTe nanobelt. (a, b) Streak camera image (a) and time-resolved PL spectra (b) of an individual ZnTe nanobelt with a pumping fluence of 5 $\mu$J/cm$^2$. (c, d) Power-dependent streak camera images (c) and the corresponding time-resolved PL spectra (d) of ZnTe nanobelt. (e) The PL lifetimes extracted as a function of power fluence. The green dashed line indicates the threshold of amplified spontaneous emission. (f) Power-dependent PL spectra of ZnTe nanobelt. (g) Intensity and peak position of PL emission as a function of pumping fluence extracted from (f) showing the amplified spontaneous emission.
Assuming that each absorbed photon can generate one electron–hole pair, the exciton density \( n_e \) can be expressed as \( n_e = \frac{F}{(\hbar \omega_{0g})} \), where \( F \) is pumping fluence.\(^{52}\) Since the pulsed width (150 fs) is much shorter than the exciton decay time constants, the diffusion of excitons is not taken into consideration. The absorption coefficient of ZnTe is \( \sim 6 \times 10^4 / \text{cm} \) (wavelength: 480 nm), which means that \( \sim 74\% \) of incident photons are absorbed by a 200 nm thick ZnTe NB with a thickness \( d \) of \( \sim 200 \text{ nm} \). \( n_{eg} \) is calculated to be \( 4.6 \times 10^{18} \text{ cm}^{-3} \), larger than Mott transition critical density of ZnTe.\(^{53}\) Therefore, we attribute the ASE of ZnTe NB in room temperature to arise from the electron–hole plasma. As the pump fluence increases above the threshold, band gap renormalization takes effect, and the band gap is lowered as a function of the carrier density.\(^{54}\) As a result, the gain is shifted towards the lower energy region and the longer wavelength modes are chosen and amplified, which can be seen in power dependence ASE peak position plotted in Figure 5g.\(^{50}\)

When the temperature \( T \) is decreased from 300 to 77 K, the free exciton lifetime increases slightly from 76 to 89 ps; however, the hot-exciton emission related lifetime increases from 17 to 20 ps, as shown in Figure 6. The increase in the free exciton recombination lifetime with decreasing temperature could be ascribed to the suppression of the nonradiative decay channels (e.g., via a phonon-mediated process to the surface states) in the nanostructures. The nonradiative decay rate due to surface states is inversely proportional to \( \exp(-E_a/\hbar \omega) \), where \( E_a \) is the activation energy for a nonradiative process.\(^5\) With a decreasing temperature, the nonradiative decay rate reduces, leading to a longer lifetime of free exciton at low temperatures. Another possible reason is that the exciton–LO phonon coupling strength is enhanced as the increasing of temperature due to the lattice expansion, leading to a shorter lifetime at high temperature.\(^{55}\) As shown in Figure 6f, the hot-exciton emission rate, highly dependent on the exciton–LO coupling strength, becomes slower with decreasing temperature, thereby fulfilling the important role of exciton–LO coupling in the exciton recombination process in ZnTe NBs.

**Conclusion.** We have investigated the exciton properties and dynamics of high quality single-crystalline ZnTe NB using time/temperature-resolved PL spectroscopy and resonant Raman spectroscopy. Free exciton and intrinsic defects, particularly Zn vacancy acceptors, determine the optical properties of ZnTe NBs. At high pumping fluence, electron–hole plasma becomes dominant and is responsible for ASE at room temperature. \( \chi_{LH} \) is strongly coupled with LO phonons, and a large number of excited electron–hole pairs release their excess energy by the hot-exciton emission process. Two time constants corresponding to hot-exciton emission and thermalized exciton recombination are identified to be 18 and 80 ps through TRPL measurement. The surface dissipation process further proves that the short lifetime is an intrinsic property of ZnTe NBs. Our results advance the understanding of excitonic radiative properties with a strong electron–phonon coupling and nonequilibrium hot-exciton emission in semiconductor nanostructures.

**REFERENCES**


**Notes**

The authors declare no competing financial interest.