REVIEWS

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Phonon-assisted upconversion photoluminescence of quantum emitters

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Abstract: Quantum emitters are widely used in quantum networks, quantum information processing, and quantum sensing due to their excellent optical properties. Compared with Stokes excitation, quantum emitters under anti-Stokes excitation exhibit better performance. In addition to laser cooling and nanoscale thermometry, anti-Stokes excitation can improve the coherence of single-photon sources for advanced quantum technologies. In this review, we follow the recent advances in phonon-assisted upconversion photoluminescence of quantum emitters and discuss the upconversion mechanisms, applications, and prospects for quantum emitters with anti-Stokes excitation.

Key words: quantum emitters; phonon-assisted upconversion; electron-phonon coupling; single-photon source

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1. Introduction

Quantum emitters in solids are the fundamental building blocks for many applications[1–7] such as lasing, light emitting diodes (LEDs), and sensing, as well as advanced quantum information processing (QIP) and communication technologies due to their advantages of robustness, ease of handling, and scalability. Common solid-state-based quantum emitters mainly include rare-earth materials[8], quantum dots (QDs)[9], color centers in diamond[10], and two-dimensional materials[11, 12]. In general, photoluminescence typically shifts to lower energies when compared to excitation energy, which is known as the Stokes shift. Photoluminescence upconversion under anti-Stokes excitation is an anomalous phenomenon that relies on the interaction of light and matter, where the energy of the emitted photon is higher than that of the laser. This has been widely used in bioimaging[13], laser cooling[14], and upconversion optoelectronic devices[15], which are the motivation for the research of PL upconversion.

In recent years, quantum emitters under anti-Stokes excitation have exhibited excellent performance. Color centers in diamonds have been widely used in quantum networks, quantum information processing, and quantum sensing because of their stable fluorescence properties and ultra-long spin coherence time[16, 17]. The spin states of nitrogen vacancy centers can be initialized by an optical method, controlled by microwave (MW), and read out by spin-dependent fluorescence detection[18–23]. By studying the emission and absorption process, Kern *et al.*[24] found that diamonds containing either NV or SiV (Nitrogen or Silicon vacancy) defects show potential for optical cryogenic cooling. Afterward, our group reported[25] the phonon-assisted upconversion fluorescence of SiV^- centers in diamond and confirmed the feasibility to achieve laser refrigeration. Later, we utilized phonon-assisted anti-Stokes excitation to control the charge states conversion of NV centers, which is critical to next-generation quantum sensing[7]. These emitters were also observed in two-dimensional (2D) materials, such as hexagonal Boron nitride (h-BN). Many important features have been reported, such as high emission brightness, and high quantum efficiency[26–31]. Deep-level defect centers with discrete electronic energy levels can act as excellent single-photon sources. However, most of these emitters suffer from severe spectral diffusion due to the fluctuating of local environment, which is detrimental to the coherence of the emitted photons. Toan *et al.*[32] demonstrate that efficient anti-Stokes excitation of quantum emitters leads to the suppression of spectral diffusion. In addition, for QDs, most studies are focused on the enhancement of the emission efficiency in pursuit of optimal single-photon sources[33]. Coherent manipulation of two-level systems not only facilitates the development of quantum light sources but also contributes to the demonstration of theoretical predictions[34–37]. Until 2021, Liu *et al.*[38] realized dual-resonance conditions in quantum-dot (QD) micropillars and improved the single photon purity. In addition, further developments may realize the reduced electron-phonon interactions and even the realization of optical refrigeration for single QDs.

In this review, we investigate recent progress in the field of phonon-assisted upconversion of quantum emitters, focusing on the excellent properties of point defects in solid-state materials. Several crucial color centers in wide-bandgap semi-

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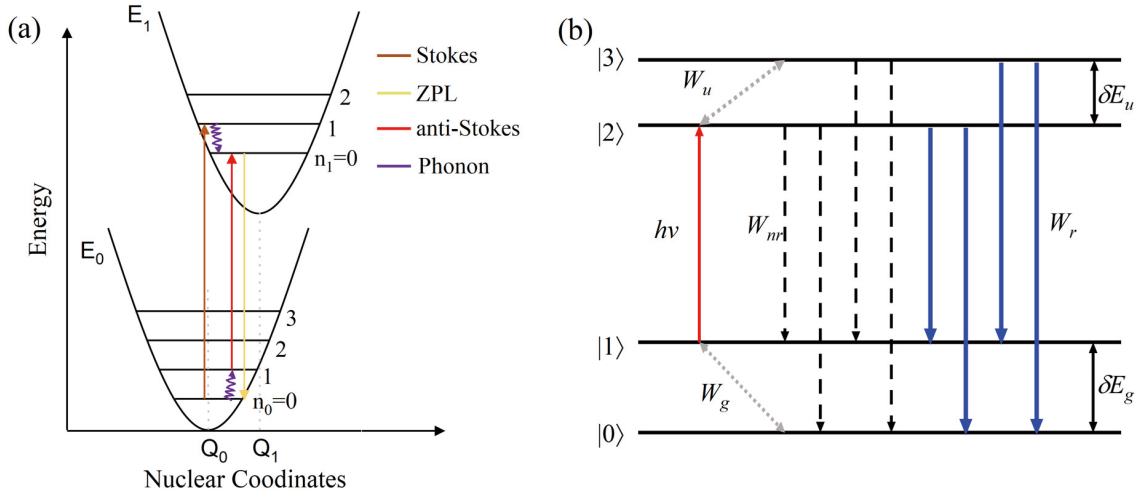

Fig. 1. (Color online) The mechanism of phonon-assisted upconversion. (a) Stokes and anti-Stokes (AS) photoluminescence processes are represented by the energy structure of electronic and vibrational levels for color centers. (b) The Simplified Model of Optical Cooling. (a) Reproduced from Ref. [10], CC BY 4.0. (b) Reprinted with permission from Ref. [40]. Copyright © 2009 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim.

conductors have been included. Among them, color centers in diamond are promising for solid-state laser refrigeration. The manipulation of the charge state of nitrogen-vacancy centers is realized by anti-Stokes excitation, which contributes to the improvement of sensitivity of quantum sensing. Furthermore, under anti-Stokes excitation, the single-photon emission performance of quantum emitters has been qualitatively improved, such as frequency stability and purity. This review provides an overview of the field of phonon-assisted upconversion photoluminescence, followed by a detailed discussion of solid-state point defects that are currently considered under anti-Stokes excitation, and finishes with a discussion of anti-Stokes excitation in the future for quantum technology.

2. The Mechanism of phonon-assisted upconversion

Stokes and anti-Stokes photoluminescence are fundamental phenomena which have been widely used to study the physical properties of materials. Stokes (anti-Stokes) photoluminescence (PL) is defined as where the energy of the emitted photons is lower (higher) than that of the laser. In the process of PL upconversion, additional energy is required to push electrons excited by low-energy photons to the conduction band or excited states. This additional energy can be gained from several processes, such as phonon absorption, multiple photon absorption, and so on. Here, we mainly focus on phonon-assisted upconversion.

Compared with multiple-photon absorption, the phonon absorption process is more efficient and is usually excited by a normal laser. The laser excites an electron from the ground state to an intermediate state. The electron then absorbs one or more phonons from the lattice and pump into the excited state. It then returns to the ground state with anti-Stokes photon emission as shown in Fig. 1(a). A photon with energy $h\nu_{exc}$ which is lower than the energy of the zero phonon line (ZPL) excites an electron from the vibrational state ($n_0 = 1$) of the ground state E_0 to the vibrational ground state ($n_1 = 0$) of an excited state E_1. The electron then returns to the ground state by spontaneous emission of a photon with mean energy $h\nu_{se} > h\nu_{exc}$. If the anti-Stokes luminescence process has high quantum efficiency, then the overall removal of phonon energy from the material may lead to laser cooling[39].

Generally, laser cooling can be understood by a simplified model. Fig. 1(b) shows the anti-Stokes process that was introduced by Seletskiy[40]. This system consists of ground-state manifold and an excited state manifold. Both have two substates |0>, |1>, and |2>, |3>. The energy gap between the ground states and excited states are δE_g and δE_u, respectively. In a semiconductor, the substates can be regarded as vibrational broadening of the ground and excited states. This model is enough, even though there are many complex substates in practice. The energy of excitation photons ($h\nu$) is resonant with the energy gap from ground-state manifold |1> to excited-state manifold |2>. The excitation process breaks the thermal equilibrium between the two manifolds. Thus, the ground and excited electrons must absorb phonons in the lattice at the rates W_g and W_u, and reach quasi-equilibrium. Afterward, spontaneous emission releases photons with the energy $h\nu_f$ into free space. The electron-phonon interaction provide support for the quasi-equilibrium of the distribution between each manifold. Generally, the interactions known as "thermalization" are much faster than the spontaneous emission rate, which is valid for most materials. The fundamentals of laser cooling processes have been discussed in more detail in earth-doped materials for laser cooling[8].

The distinct feature of phonon-assisted photoluminescence (ASPL) upconversion is that the process is temperature sensitive. As the temperature increases, the intensity of the ASPL increases because there are more available phonons[41, 42]. In contrast, the intensity of Stokes PL decays with temperature due to the increase of nonradiative transitions[43]. Therefore, temperature-dependent ASPL and the Raman spectra can be utilized to precisely identify the phonon modes involved in the upconversion process[44–46].

Another characteristic of ASPL is the linear dependence of laser power. Their relationship can be expressed as the equation $I = bP^n$, where I is the PL intensity, P is the excitation power, b is a constant, and n is an exponent. When the power is lower, the ASPL increases almost linearly ($n \approx 1$) with

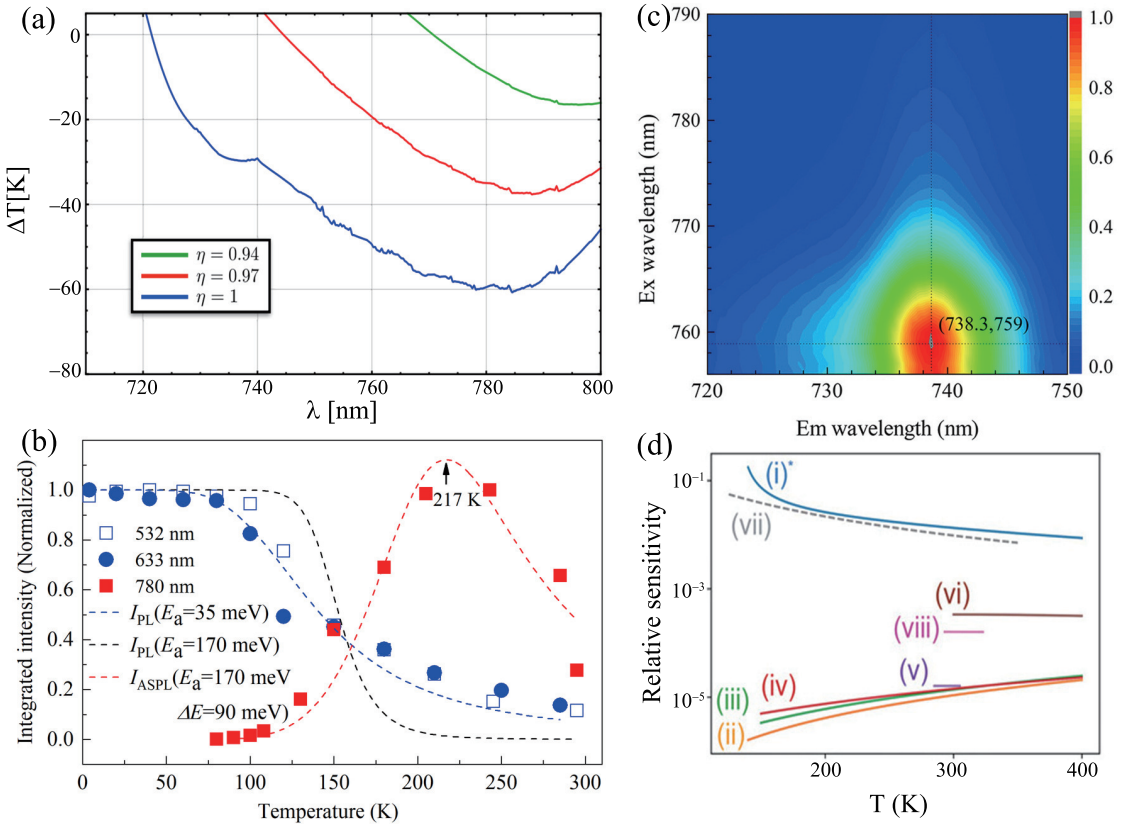

Fig. 2. (Color online) Phonon-assisted upconversion photoluminescence in diamond. (a) Cooling of an NV-doped diamond suspended in vacuum. The cooling temperature as a function of quantum efficiency. Here it is assumed that non-radiative process heats the diamond. (b) The temperature dependence of intensity under Stokes and anti-Stokes excitation for SiV^- centers. (c) Anti-Stokes PLE spectra of SiV^- centers (ZPL: 738 nm) at room temperature. (d) Characterization of the anti-Stokes-based nanothermometer: the relative sensitivity versus temperature for several different systems. (a) Reprinted with permission from Ref. [24]. Copyright © 2017, American Physical Society. (b) and (c) Reprinted with permission from Ref. [25]. Copyright © 2018, American Chemical Society. (d) Reproduced from Ref. [10], CC BY 4.0.

power[47]. Further increases in the laser power saturates the available states, and the ASPL intensity increases sub-linearly with the increasing laser power[41].

3. The ASPL of quantum emitters for laser cooling

Phonon-assisted upconversion of quantum emitters has been reported in diamond, 2D materials, and QDs. In this section, anti-Stokes excitation of quantum emitters and their excellent performance in practical applications will be reviewed.

3.1. Color centers in diamond

Over 100 kinds of optically active color centers in diamonds have been reported, and a lot of research has been devoted to applications such as quantum computing, quantum information processing, temperature, pressure, magnetic metrology, and super-resolution microscopy[6, 48–50].

Recently, Kern *et al.*[24] reported the models of silicon-vacancy (SiV^-) and nitrogen-vacancy (NV^-) centers for optical refrigeration and suggested that it is possible to achieve net cooling in microdiamonds (<200 μm) which is analogous to RE-doped materials[51]. When the quantum efficiency is close to unity, the theoretical model predicts that using the SiV^- (NV^-) color center as a refrigeration medium can reduce the temperature by 21 K (60 K) from room temperature. Systematic studies of quantum efficiency have found that small reductions lead to dramatic changes in cooling effect as shown in Fig. 2(a). In a vacuum, an excitation power of 100 mW is sufficient to produce a temperature reduction of 10 K for suspended microdiamonds. In the model, suppression of nonradiative relaxation is key to achieving net cooling. The levitated microdiamond was utilized for laser cooling due to its thermal isolation. In addition, cryocooling requires color centers with high quantum efficiencies. It has been experimentally demonstrated that the NV color centers in nanodiamonds have very high quantum efficiencies[52]. Notably, the temperature changes can be characterized using standard optical spectroscopy techniques. These results will promote the experimental study of laser cooling of diamonds, which is expected to observe solid-state laser cooling in diamonds in the future.

Afterward, our group experimentally observed the ASPL of the SiV^- centers[25]. By analyzing the dependence of ASPL on temperature, pump power, and excitation energy, we confirm the existence of phonon-assisted photoluminescence upconversion and obtain optimal excitation wavelength at room temperature. Fig. 2(b) shows the temperature dependence of the intensities of Stokes excitation (532, 632.8 nm), and the anti-Stokes excitation (780 nm). Consistent with this discussion, the ASPL intensity increases exponentially with temperature between 80 and 217 K. In contrast, for the Stokes excitation, their intensities are almost unchanged from 4 to 100 K and decrease rapidly with temperature from 100 to 300 K. The ASPL intensity is determined by the average number of phonons and the recombination rate of electron–hole pairs.

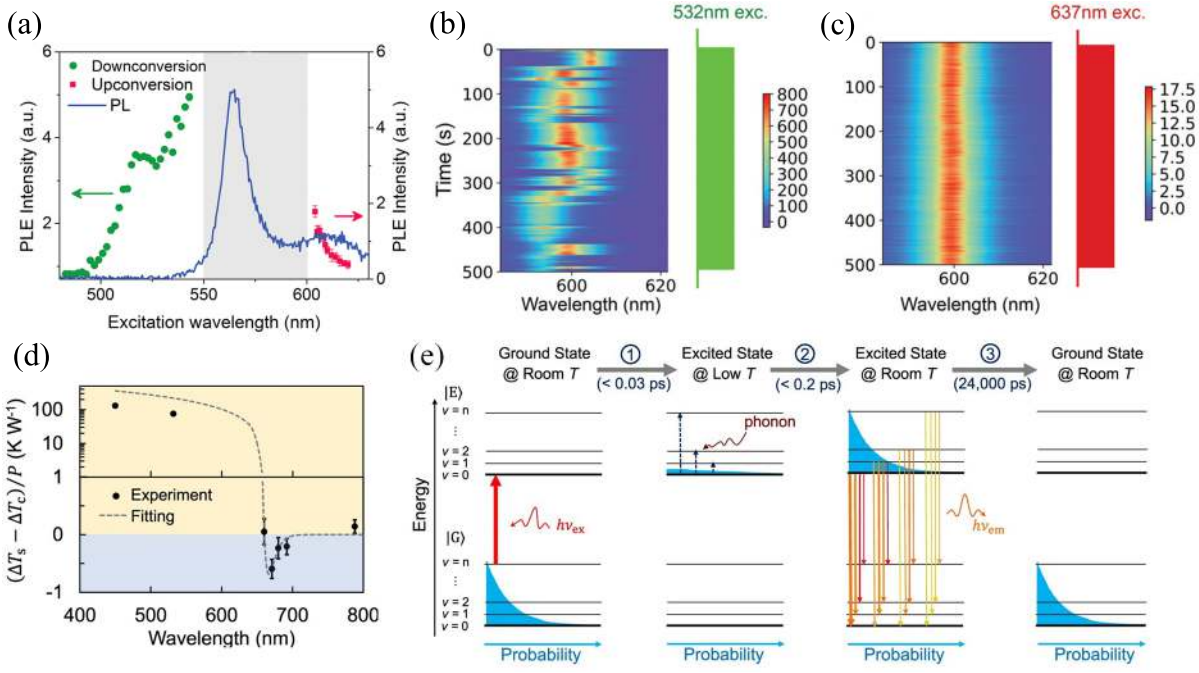

Fig. 3. (Color online) Photoluminescence upconversion in low dimensional materials. (a) The photoluminescence excitation spectrum of the integrated ZPL (565 nm). The green dots and red squares correspond to Stokes and anti-Stokes excitations, respectively. The suppression of spectral diffusion under anti-Stokes excitation: the PL time series of a single emitter under (b) Stokes excitation (532 nm) and (c) anti-Stokes excitation (637 nm), respectively. The optical cooling of QDs. (d) The temperature changes of the QD sample under different excitation wavelengths. (e) The upconversion photoluminescence mechanism of QDs. (a) Reproduced from Ref. [43]. Copyright © 2018, American Chemical Society. (b) and (c) Reprinted with permission from Ref. [32]. Copyright © 2019, AIP Publishing. (d) and (e) Reproduced from Ref. [64], CC BY 4.0.

As the temperature increases, the average phonon number increases, while the external quantum efficiency decreases. Therefore, the ASPL strength mainly depends on their product[14]. We then performed anti-Stokes PLE measurements to explore the phonon modes that are mainly involved in the upconversion process as shown in Fig. 2(c). The ASPL intensity reaches the maximum when the photon energy is 50 meV red-detuned below the zero-phonon line, which indicates there is a resonant mechanism. A similar resonance-enhancing process was observed in previous experiments in which semiconductor laser refrigeration was achieved for the first time in CdS nanoribbons. This process is critical to achieve net laser cooling[14].

Limited by the low external quantum efficiency in bulk diamond, no net cooling is observed in our experiments. However, this process grows exponentially with temperature, which is of great interest in fundamental research such as cavity quantum electrodynamics[53, 54] , bioimaging[55] , and Raman spectroscopy[56]. Anti-Stokes photoluminescence is generally inefficient, so most studies of phonon-assisted upconversion fluorescence of color centers use high-concentration samples[43]. Tran *et al.*[10] reported that anti-Stokes excitation of color centers in diamond is an efficient process, and they realized an all-optical nanoscale thermometer based on the sensitive dependence of the anti-Stokes to Stokes PL intensity ratio on temperature. Fig. 2(d) shows the excellent performance against other schemes. This graph shows the sensitivity of various advanced nano-thermometry techniques. The relative sensitivity is based on (i) anti-Stokes to Stokes PL intensity ratio, (ii) and (iii) the frequency shift reported[6] , (iv) the ZPL wavelength shift of the SnV[57] and (v) SiV^- centers[58] , and (vi) the intensity changes of the NV centers[59]. To date, their technique is superior to several other methods, and is comparable to previous methods by the ratio of Stokes and anti-Stokes intensities in Raman spectroscopy[60]. In general, other methods are similar in sensitivity for some cases, but usually have some disadvantages, such as temperature response range and environmental limitations. Their results provide an important way to study the fundamental interactions in a single quantum system, not only for defect centers, but also for quantum dots systems.

3.2. The upconversion in low-dimensional materials

Compared with bulk diamonds, low-dimensional materials have intrinsic advantages in optical refrigeration applications, such as external quantum efficiency. The intrinsic light emission of h-BN is in the ultraviolet range due to its large bandgap (6 eV)[61]. Like diamond, the wide bandgap can provide an innate environment for the formation of defect centers in the visible light range. Because of the strong coupling between the defects and the lattice, larger phonon sidebands (PSBs) appear in the emission of h-BN defect states. Wang *et al.*[43] reported PL upconversion in h-BN. Fig. 3(a) displays that the PLE spectra of Stokes excitation and anti-Stokes excitation are almost symmetric relative to the ZPL (565 nm). The energy gain in the PL upconversion process is about 162 meV which is consistent with the optical phonon energy. This experiment demonstrates the strong defect-phonon coupling in h-BN, which provides the possibility for laser refrigeration in 2D materials. Unfortunately, no further research has been done on laser cooling.

The emission from solid-state quantum emitters often suffers from spectral diffusion or jitters[62]. This is mainly related to localized charge fluctuations near the quantum emitter. The local electric field variation causes a small shift in the en-

ergy of the emitted photon through the Stark effect. High energy excitation can easily cause charge transfer and ionization process, leading to obvious changes in the local environment of the quantum emitters, thus affecting the radiation process of the quantum emitters, especially the dynamic Stark effect caused by the local electric field changes the energy level structure. Low energy excitation can minimize the charge transfer and ionization process, thus reducing spectral diffusion. Figs. 3(b) and 3(c) show the PL for a single point defect under Stokes excitation and anti-Stokes excitation, respectively. They found that under Stokes excitation, the emitter exhibited severe spectral diffusion and jitters, while almost no diffusion occurred under anti-Stokes excitation, even with higher laser powers. Therefore, this experiment demonstrates that the phonon-assisted upconversion process can be used to mitigate spectral diffusion. The authors believe that the main reason for the suppressed spectral diffusion is that the laser energy is lower than the activation barrier of the localized charge defects near the emitters. Simultaneously, the absence of spectral diffusion indicates that upconversion can be used for tuning the emission wavelength of solid-state quantum emitters. Their results also provide a feasible way to tune the emission wavelength of solid-state quantum emitters and provides important insights into the physical properties of quantum emitters in h-BN. Afterwards, Wigger *et al.*[63] systematically studied the phonon-assisted absorption and emission spectra of the individual color centers in h-BN, confirming that the excitatiion of the emitters is most effective by LO-phonon assisted absorption, which leads to a deeper understanding of the fundamental properties of color centers in h-BN.

In addition to two-dimensional materials, QDs also exhibit excellent optical properties under anti-Stokes excitation. Traditional organic dyes and rare-earth-doped materials show excellent performance in laser refrigeration applications[54], but there are shortcomings of poison and cooling limitations. Although bulk semiconductors can overcome these shortcomings, they are technically prohibitive to reaching extremely low concentrations of nonradiative recombination centers for efficient ASPL under ordinary excitation. In addition, bulk semiconductor with high index of refraction captures emitted photons, leading to strong reabsorption. The size of QDs in the quantum confinement regime has been explored for upconversion photoluminescence. The generally accepted physical mechanism relies on thermal activation of defect states in the band gap. This means that the up-conversion process is generally inefficient. A few publications have reported[14] semiconductor nanomaterials with high power-conversion efficiency under sub-bandgap excitation, but the mechanism has been debated in the recent literature[65]. Recently, Ye *et al.*[64] reported that the upconversion photoluminescence efficiency for CdSe/CdS core/shell QDs is beyond unity. They then performed the characterization of laser refrigeration. As shown in Fig. 3(d), after subtracting background heating, Stokes excited QDs show a strong excitation wavelength-dependent heating effect. In sharp contrast, excitation at 660 nm significantly reduces the heating effect. When the excitation wavelength is further shifted to long wavelength (671 nm), the maximum temperature drop can reach 0.18 K under 300 mW excitation.

Unlike the defect-assisted upconversion photoluminescence for colloidal QDs, single-dot spectroscopy reveals that the same electro-phonon coupling states are involved in anti-Stokes photoluminescence and Stokes photoluminescence. Characterization of the transition process by ultra-fast spectroscopy implies that under anti-Stokes excitation, the thermalization of excitons is greatly accelerated and formed within 200 fs, which is 100 000 times faster than the radiative recombination rate of excitons. The ASPL mechanism of the high-quality QDs is shown in Fig. 3(e). At room temperature, electrons are populated over the electron-phonon coupled states (v) on the ground state. Within 0.03 ps, low-energy photons promote the electron at the ground state |G> to the bottom of the excited state |E> process at room temperature. This phonon-assisted absorption process produces an intermediate state, which can be thought of as a statistical thermodynamic 'low temperature' distribution. Then, the intermediate state relaxes to a 'room temperature' quasi-equilibrium distribution. Finally, there are few non-luminescence defects of band-edge excitons, and the quasi-equilibrium distribution is mainly completed by emitting high-energy photons through the radiation transition process, and the quantum efficiency is close to unity. These results demonstrate that QDs can serve as efficient, stable, and cost-effective emitters for phonon-assisted upconversion photoluminescence in various applications.

4. Anti-Stokes excitation in quantum science

The last section has shown that quantum emitters under anti-Stokes excitation exhibit excellent performance in laser refrigeration. In addition, combined with their applications in quantum sensing and quantum information processing, the performance is also outstanding. In this section, we will discuss the application of quantum emitters in quantum science under anti-Stokes excitation.

4.1. Anti-Stokes excitation for quantum sensing

The color centers in diamonds are potential candidates for next-generation solid-state quantum devices due to their excellent optical properties. Being in a spin-free lattice, the negatively charged NV^- centers exhibit ultralong spin coherent times even at room temperature in solid-state systems[66]. The reported experiments show that ultra-high sensitivity detection of the external electric field and magnetic field can be performed by manipulating and reading the spin state of the NV color center. Currently they have been used for high-speed quantum electronic devices, nanoscale magnetic detection, and temperature sensing[67, 68]. To improve the sensitivity and the signal-to-noise ratio (SNR) of NV^- based quantum devices, a high concentration of NV^- centers is required. However, the neutral charge state (NV^0) is usually located near the surface. Several methods have been used to solve this problem[19, 69, 70] , such as controlling the growth process, surface hydrogenation, and electric manipulation. In contrast, the optical control method is convenient and reversible.

The charge dynamics of NV centers can be understood by the energy diagrams that follow. Usually, the charge state transition can be accomplished by absorbing two photons in succession. The first photon pumps the electron in the ground state to its excited state, and the second photon promotes the excited electron into the conduction band, then the NV^- loses the electrons it carries and converts to the neut-

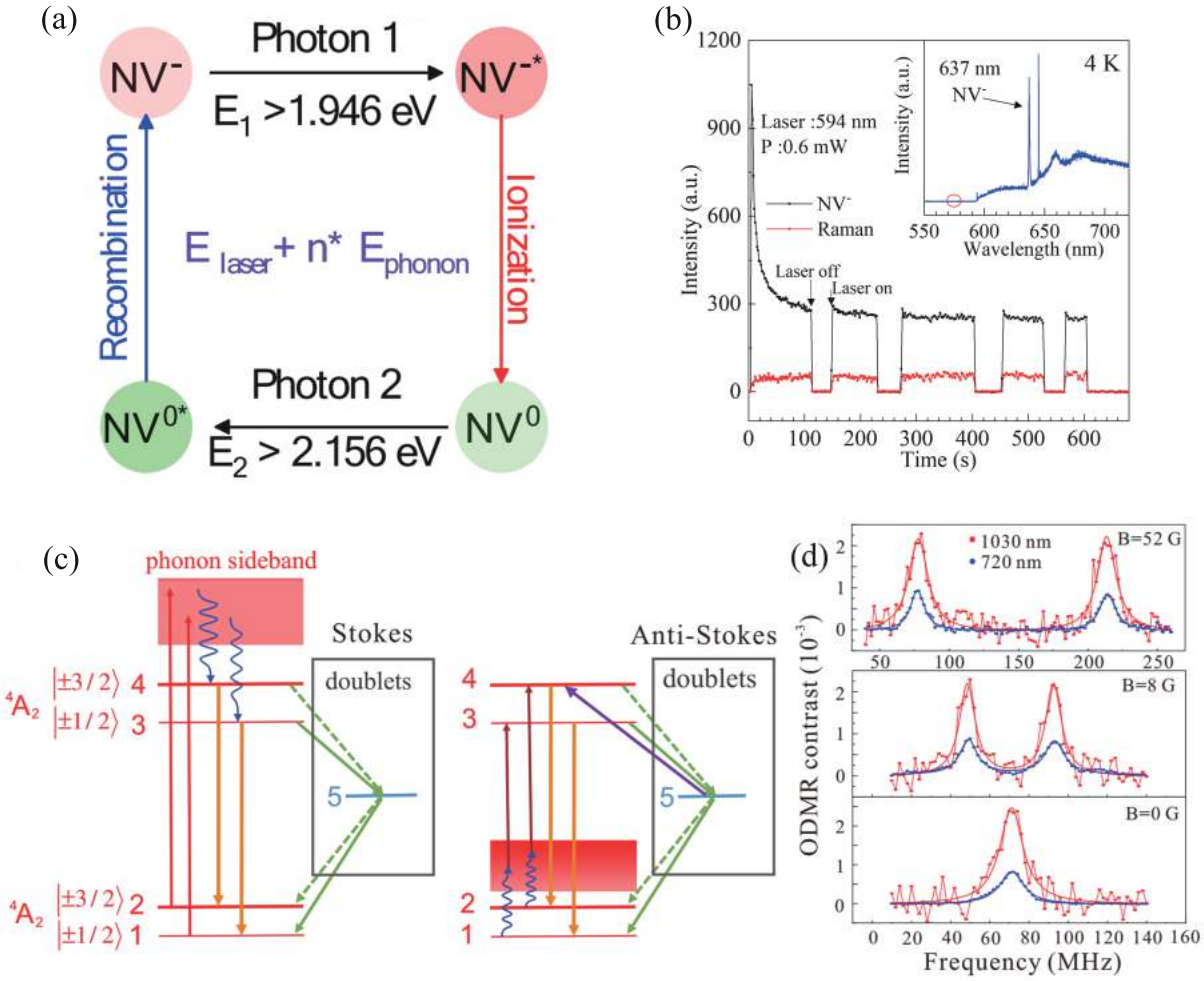

Fig. 4. (Color online) Quantum sensing under anti-Stokes excitation. (a) Charge state manipulation of NV centers: the charge state conversion process between NV^0 and NV^- under different excitation wavelengths. (b) The decay process of NV^- centers at 4 K under anti-Stokes excitation. Robust coherent control of spin qubits using anti-Stokes excitation. (c) The excitation schemes of V_{si} center under Stokes excitation and anti-Stokes excitation. (d) Stokes and anti-Stokes excited ODMR of V_{si} centers for different external magnetic fields. (a) and (b) Reprinted with permission from Ref. [7]. Copyright © 2022, American Chemical Society. (c) and (d) Reproduced from Ref. [72], CC BY 4.0.

ral state NV^0. Similarly, NV^0 can convert back to NV^- by a two-step process involving the absorption of a photon with energy to push the hole into the excited state, and then the second photon excited the hole to the valence band[71].

Through an understanding of the above charge state transition mechanism, we found that the charge state conversion is mainly dependent on the excitation wavelength. Therefore, we propose to use phonon assistance to compensate for the lack of energy in the anti-Stokes excitation process, thereby changing the conversion rate between the two charge states, as shown in Fig. 4(a). Then, our group experimentally utilized phonon-assisted anti-Stokes excitation to control the reversible conversion between the NV^0 and NV^- states[7]. Furthermore, we also investigated the dynamics of spectral structure evolution, and we found that, the spectral structure of the NV color center undergoes spectral diffusion over time under anti-Stokes excitation. The PL spectra under anti-Stokes excitation are shown in Fig. 4(b). There is no PL signal from neutral state NV^0 observed at low temperatures. Meanwhile, during the whole measurement process, we observed that the luminescence intensity of the negatively charged state NV^- gradually decayed and finally stabilized. In addition, at low temperatures, the saturation of NV^- appears, and it gradually changes to a linear dependence on the laser power with temperature up. This reveals that the neutral charge state is converted to the negative charge state as the upconversion takes place. Our results demonstrate that anti-Stokes excitation provides an alternative method to control the charge state conversion process. Point defects in wide-bandgap semiconductors have been used in quantum information processing. Generally, only a specific charge state is selected for utilization. Therefore, the control of charge states must be considered. Anti-Stokes excitation to manipulate the charge state can be used not only for NV centers in diamond but also for h-BN. In addition, the conversion of charge states needs to be considered in laser refrigeration, which is neglected in the current research, and it may have a qualitative effect on the cooling efficiency.

The field of quantum sensing only takes advantage of the fact that the spin state can be read by the optical method. However, the coherent control of spin for quantum information processing and quantum computing is more attractive. Optically detected magnetic resonance (ODMR) technology is significant for applications of quantum technology[73–75]. Recently, Wang *et al.*[72] propose to use anti-Stokes excitation to detect the ODMR signal in silicon carbide (SiC), and they sys-

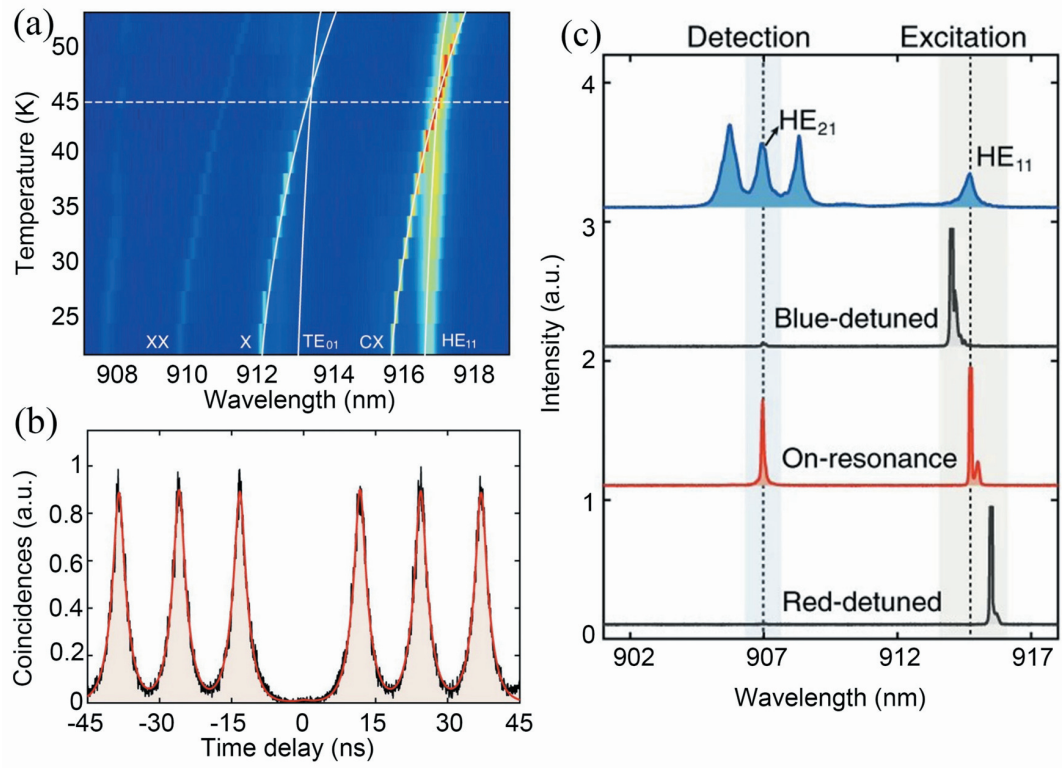

Fig. 5. (Color online) The single-photon source under anti-Stokes excitation. (a) Dual-resonance enhanced X-CX transition for highly pure single-photon emission. Temperature-dependent PL mapping of a QD in cavity. (b) Hanbury Brown and Twiss (HBT) measurements of single-photon purity under the dual-resonance enhanced intra-dot excitation. (c) Dual resonances enhanced upconverted excitation. (a)–(c) Reproduced from Ref. [38], CC BY 4.0.

tematically studied the entire upconversion process, including laser power, microwave power, and temperature dependence. They demonstrate that the ODMR contrast under anti-Stokes excitation is several times that of the Stokes excitation and realized coherent control of spin at room temperature. They proposed the theoretical model and optically induced spin polarization under Stokes and anti-Stokes excitation of V_{si} defect as shown in Fig. 4(c). The defect has $S = 3/2$ spin states with an excited state ($^4A_2$) which has $m_s = \pm 1/2$ and $m_s = \pm 3/2$ spin manifolds. In general, the phonon relaxation and absorption processes should be spin-conserving (spin-independent). Through phonon relaxation, they rapidly thermalize to the "3" and "4" which is the substates in the excited states, then the excited electrons relax to the ground states by the spin-preserving radiative process. Under anti-Stokes excitation, the probability of pumping from the ground state manifold to the excited state manifold is less, because the phonon absorption is involved. However, the non-radiative process to the meta-stable state occurs primarily from state "3", then they polarized to state "1"[76]. Under anti-Stokes excitation, a spin-flipping excitation process (the purple arrow) from the meta-stable state to the state "4" occurs, which makes a qualitative difference.

After optimizing the anti-Stokes excited ODMR spectrum, the authors studied the magnetic field-dependent behavior. Fig. 4(d) exhibits the Stokes and anti-Stokes excited ODMR spectra. The laser powers for Stokes and anti-Stokes excitation are set at 1 and 14 mW, respectively, while the MW power is set to be the same. Both ODMR spectra excited by Stokes and anti-Stokes show the same splitting, however, it is observed that the contrast under anti-Stokes excitation is approximately three times that under Stokes excitation. Furthermore, they found that at high temperatures, the ODMR signal under anti-Stokes excitation is also more robust than the Stokes excitation, which is more suitable for quantum technology at high temperatures. Their results provide a direction for developing anti-Stokes excitation in quantum information processing and quantum sensing.

4.2. Anti-Stokes excitation for single-photon sources

The previous section showed that the jitter of frequency of single-photon emission in h-BN can be suppressed under anti-Stokes excitation. Besides the frequency jitter of the single-photon emission, many types of research have focused on improving the performance through optical microcavities.

In the past decade, significant progress has been made in nanophotonics by exploiting enhanced light-matter interactions in optical microcavities. For example, enhancement of scattering, the realization of sensitive detection at the single molecule level, and efficient nonlinear effect. However, most nanophotonic devices are based on high-quality dielectric microcavities. It would be ideal if both the excitation and emission processes resonated with the cavity modes, but it is technically challenging, especially for high-Q factor microcavities. Dual and even triply resonances conditions have been achieved in photonic crystal cavities, micro-rings, and micro-spheres, which leads to unprecedented device performances[77–79].

Recently, Liu *et al.*[38] reported that optical resonance in a quantum dot (QD) micropillar system facilitates both excitation and emission processes and improves single photon purity. In addition, the rare upconversion process at single-

photon level was observed under dual resonance conditions. As shown in Fig. 5(a), they experimentally achieved dual resonance by adjusting the temperature. When the sample temperature is changed, the emitted photon energy shifts. The microcavity is affected by the temperature, so the cavity modes also shift. Since the emitted energy shifts faster than the cavity mode, both the quantum dot and the cavity mode can reach resonance at the same time. According to the temperature-dependent spectra, the X and CX states are simultaneously resonant to the TE_{01} and HE_{11} modes respectively. In Fig. 5(b), under the dual-resonance excitation, the coincidence event $g^2(0)$ is almost disappears in the entire histogram. Afterwards, they explored the physical mechanism of the double resonance excitation process, which they believe is mainly due to the suppression of carrier reprocessing in the semiconductor, resulting in the generation of high-purity single photons. Quantum dots under high energy excitation has the carrier recapturing process in the relaxation process, but the dual- resonance excitation process can change the transition path and inhibit the recapture process of the carrier, so this process can achieve high-purity single photon emission. In contrast to the dual-resonance enhanced down-conversion process, it is also feasible to utilize the fundamental mode to enhance the optical excitation and utilize the high-order cavity mode to enhance the unconverted photon emission. As shown in Fig. 5(c), under the dual-resonance condition, bright X state emission is observed while the emission almost disappears once the laser is slightly detuned from the HE_{11} mode.

Their results can be employed to cool the mechanical resonator to its quantum ground state, which shows great potential in exploring fundamental quantum physics[80]. Further developments in this direction may lead to the realization of optical refrigeration for single QDs. In addition, the QD micropillar system under dual-resonance excitation can be used as an ideal solid-state system to study the interaction of quantum systems and develop quantum functional devices.

5. Challenges

Quantum emitters under anti-Stokes excitation have been investigated. Compared to Stokes excitation, there is a significant disadvantage of the low efficiency. Therefore, more research is needed to improve the upconversion efficiency. The efficiency of the upconversion process can be greatly increased by intermediate states. The main reason of this is that the increase in the density of intermediate states can greatly improve the absorption cross-section. An important direction in the future is to artificially design the intermediate states of materials, thereby increasing the efficiency of upconversion luminescence. For QDs, new fabrication methods, such as doping, can be developed to control the stoichiometry of the material, thereby introducing intermediate states. Increasing the radiative recombination rate is another important way to improve the upconversion efficiency. Combining defect centers with optical microcavities and increasing the radiative transition rate through the Purcell enhancement effect is a universal method, which could be improved through changing the emission pathways associated with the Purcell enhancement inside a cavity. Meanwhile, Purcell enhancement of the ZPL has two advantages: (1) relative to the ZPL which does not create any phonons, the emission on the PSB is reduced; and (2) the optical lifetime is shortened, strengthening the radiative decay pathways, which increases the quantum efficiency. Resonating with multiple cavity modes while satisfying excitation and emission enhancement is an important direction for future research.

In addition to looking for methods to optimize the upconversion efficiency, the investigation of quantum emitters under anti-Stokes excitation will open new areas of research in quantum sensing and quantum computing. Anti-Stokes excitation can change the transition process of electrons and reduce the jitter of single-photon emission frequency. However, the charge state of the color center is critical for its application. Anti-Stokes excitation provides a feasible scheme to control the charge state of quantum emitters. This applies not only to color centers in diamond but is also suitable for points defects in other materials.

6. Conclusions

We have reviewed the fundamental properties of quantum emitters under anti-Stokes excitation, including color centers in wide-bandgap semiconductors and QDs. They have all proven to be promising for net cooling. However, using color centers to achieve laser cooling has so far remained a prominent experimental goal. We then discussed the application of anti-Stokes excitation in quantum sensing and single-photon sources. The contrast of ODMR can be improved under anti-Stokes excitation, and the frequency stability and the purity of the single-photon emission are qualitatively improved, which is crucial for the development of quantum technology in the future. Finally, we outline an important future research direction, focusing on quantum emitters under anti-Stokes excitation for quantum information processing and quantum computing.

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