Anomalous nonlinear optical effect and enhanced emission by magnetic excitons in CVD grown cobalt-doped ZnSe nanoribbon

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Abstract
The magnetic excitons in diluted magnetic semiconductor (DMS) have varied formats due to the inhomogeneous phases out of doping concentration and/or structural relaxations or defects. Here the high quality cobalt-doped zinc blende ZnSe nanoribbons (NRs) were synthesized, showing bright and color-variable emissions from blue, yellow to a little mixed white colors. Their power and temperature dependent micro-photoluminescence (PL) spectra have been obtained in which two emission bands, one magnetic exciton band near the band-edge and a Co2+ high-level d–d transition emission band at 550 nm out of their ferromagnetic (FM) coupled aggregates in ZnSe lattice, both bands could also be reflected by a nonlinear optical absorption enhancement. The easy formed stacking fault defects in a chemical vapor deposition (CVD) grown ZnSe zincblende NR took part in the above optical processes out of magnetic polaronic excitons (PXs). The femtosecond (fs) laser pulse pumping on single ZnSe:Co NR produces obvious lasing behavior but with profile of a complicated magnetic exciton interactions with indication of a crossover from collective exciton magnetic polarons (EMP) to bound magnetic polaron (BMP) scattering in Co doped ZnSe NR. These findings indicate the complication of the magnetic coupling natures in varied DMS structures, whose optical properties have been found to be highly nonlinear, due to the involvement of the spin–spin, spin–exciton and spin–phonon interactions, verified by the theoretic calculation in Yang X-T et al (2019 Interstitial Zn-modulated ferromagnetism in Co-doped ZnSe Mater. Res. Express 6 106121).

1. Introduction
The bright, color variable luminescence of semiconductor often has related to the modulation of their composition and electronic states in them [1–3]. Nanocrystals, nanoribbons and nanoplate have been the focus in this field upon their sizes and shapes [1, 4–6], also the environments they stay and their aggregation states [7, 8] especially the nanoribbon (NR) can also work as active waveguide or optical cavity for the coherent light generation, propagation and amplification [9, 10]. There have been many reports on...
tunable luminescence materials and their variable photonic responses by energy band modulation in doped NRs [1] and doped QDs [11]. MAK et al found the emission peak shift from 570 nm to 850 nm due to the ferromagnetic (FM) spin coupling of aggregated Mn ions in Mn-doped wurtzite (WZ) CdS nanowires [12]. The d–d radiation transition at 640 nm out of the aggregated Mn$_1$ cluster in wurtzite ZnO:Mn nanowire [13] have been identified by the time-delayed PL spectra. In Mn ion or Co doped wurtzite CdS nanowire the LO phonon coupling and FM spin–spin coupling to free exciton (FX) combine to form exciton magnetic polaron (EMP) and localized EMP (LEMP) to dominate their emission and producing the bosonic lasing from collective EMPs in DMS structures [14, 15]. However, the Mn(II) doped zincblende (ZB) nanostructure gives even complicated optical properties [16, 17]. Besides the EMP, another excitation AMP [18] or bound magnetic polaron (BMP) [19] due to the interaction between antiferromagnetic (AFM) coupled TM ions and free exciton could also form and determine their optical properties. Both EMP and BMP could coexist to give their emission. How these excitations form, and why a different optical behavior in a zincblende ZnSe nanostructure occurs from a doped wurtzite nanostructure needs careful study.

Another important application of NR is the amplification of its luminescence for nanolaser. Since nanolaser was first reported by Yang group in ZnO NRs at 2001 [20], various lasing profiles have been observed in such as CdS NRs [21], GaN NRs [22], lead halide perovskite NRs [23], and other materials [24, 25], due to the exciton–exciton coupling, or electron–hole plasma or the exciton–polariton in their semiconductor nanostructures. It is interesting that the bosonic lasing due to the collective EMPs in DMS nanostructures [14, 15, 26] have been proposed be related to the multi-stable magnetic exciton polaritons [27], therefore sometimes dual lasing lines with large span could be produced by delocal and local collective EMP or magnetic exciton polariton simultaneously [15]. So spin-oriented excitons or magnetic polarons at high excitation in different DMS nanostructures are very important excitations with potential applications, for example, the photocatalysis in Mn doped QDs [28], bosonic laser by exciton polariton condensate [29], deserve to be studied further. These micro-nano materials demonstrate attractive nonlinear optical properties that could find great impacts in the future of nanolasers or other photonic devices.

Zinc selenide ZnSe is a direct bandgap semiconductor (e.g. ~2.67 eV), which has been deemed as a great blue light emitting material in late twentieth century based on high quality sample, easy grown process and chemical inertness, while its short fluorescence lifetime seriously affects their applications in optical devices [30, 31]. For the chemical vapor deposition (CVD) growth, zincblende ZnSe NR or belt often show multi-layers of stacking fault in the wire, which cause significantly redshifted emission band out of deeptrap [32]. Moreover, ZnSe has also been thought to be an important spintronic material after TM ion doping, whose enhanced spin Hall effect in ZnSe:Cl [33] and anomalous Hall effect in ZnSe:Mn [34] have been observed. The micro-PL spectra of single ZnSe:Mn belt show clear d–d transition emission bands at close locations from single Mn ion, the AFM and ferromagnetic (FM) coupling Mn ion pairs, while the AFM coupled Mn pair is strongly related to the presence of ordered defects [17]. Importantly, Co(II) is an important transition metal (TM) ion dopant in diluted magnetic semiconductors (DMSs) and oxides, with seven d electrons, which can hybridize with s and p electrons of anion of the host semiconductor to give rise to lots of interesting luminescence, electrical, and magnetic properties [35], especially the infrared emission by local d–d transition [36] and nonlinear optical absorption [37, 38]. In cobalt doped ZnSe DMS, Co$^{2+}$ ion not only introduces the magnetic properties into NRs but also modifies their optical emission properties in visible region [39]. Though these findings how the magnetic coupling of Co ions in ZnSe lattice modulates their optical property is still unclear so far.

In this paper, we successfully synthesize high quality cobalt doped ZnSe NRs by vapor–liquid–solid method and analyzed the luminescence characteristics by studying their steady-state micro-PL spectra and PL lifetimes, observed bright, color-variable and very long-lifetime luminescence. Femtosecond (fs) laser pulse pump produces obvious anomalous lasing behavior, indicating a potential excellent blue tunable lasing material, with attracting magnetic coupling profiles.

2. Experimental section

Cobalt-doped ZnSe NRs were synthesized by an Au-catalyzed CVD method as follows. The mixed powders of high-purity ZnSe (Alfa Aesar, 99.99% purity) and cobalt hydroxide (aladdin, 99.9%) with mass ratio 10:1 loaded in the ceramic boat were inserted into the central region of the quartz tube, which is mounted in a tube furnace. The cleaned silicon substrates coated with ~10 nm thick Au layer were placed in the down stream away from the central region of quartz tube of about 10 cm. Before growth of the samples, the quartz tube was purged with mixed gas of 95% argon and 5% hydrogen for 1 h. Then the mixed powders were heated to 1150 °C at the rate of 85 °C min$^{-1}$ and hold for 120 min at this temperature for samples growth. When experiment finished, furnace was cooled down naturally to room temperature and obtained
yellow colored product on silicon wafers. During the experiment, the mixed carrier gas was kept flowing at ~40 standard cubic centimeters per minute.

The morphology of as-synthesized samples was characterized by a field-emission scanning electron microscope (FE-SEM, Zeiss SUPRA 55) equipped with energy dispersive spectroscopy (EDS). Photoluminescence (PL) spectra were measured by laser confocal PL microscope system (Princeton Instruments Acton SP2500) using continuous laser with wavelength 405 nm as the excitation source. Temperature-dependent PL spectra (77–300 K) were performed using a liquid-nitrogen-cooled cryostat system (Janis ST-500, Microscope Cryostat). PL lifetime measurements were recorded by the time correlated single-photon counting system (Picoquant 'Timeharp 200') at different emission wavelength. The pulsed diode laser (Picoquant 'PDL800-B', 10–80 MHz) with wavelength 405 nm (tens of ps pulse-width) was used as the excitation source. Ti-sapphire laser (coherent) equipped with wavelength tunable instrument was used to pump NRs emission lasing (pump wavelength 405 nm, repetition rate 1 kHz, pulse length ~100 fs). All the optical experiments were done under the microscope system (Olympus BX51M, an objective lens 50×). The facility of x-ray photoemission spectroscopy is XPS/INA-X by Specs Company. Powder x-ray diffraction (XRD) measurements with Cu Kα radiation were performed using SMARTLAB3KW diffractometer. The Raman spectrum was characterized by WITEC alpha300R Raman fluorescence spectrometer with a 532 nm laser as an excitation source. The magnetic properties have been obtained on the MPMS (SQUID) XL-7 from Quantum Design.

3. Results and discussion

A representative SEM image of as-prepared Co(II)doped ZnSe NRs is clearly demonstrated in figure 1(a).

The diameters of the NRs can reach several 10 μm and the length can reach 100 μm. Figure 1(b) shows SEM image of an individual NR with smooth surface and irregular shape, which is confirmed by the high magnified SEM image shown in the inset. The energy dispersive spectrometer (EDS) mapping of an individual Co doped ZnSe NR is shown figure 1(c), which verifies that there are three elements Co, Se and Zn in this NR, and the EDS mapping indicates that the inside Co ions are almost uniformly distributed in the NR. Figure 1(d) shows the EDS elemental content of Zn, Se and Co to be 49.73%, 49.20% and 1.07%, respectively. It can also be seen that the elemental content ratio of Zn to Se in NRs is over 1 slightly, which is all ferromagnetism but its optical properties is in contrast to that the dominant BMP formation due to AFM coupling between Co ions in heavy Zn content (Zn:Se = 1.1–1.15) in that ZnSe:Co nanowire [19].

The x-ray photoemission spectroscopy has been obtained as shown in figure 2 in which includes the full XPS spectra of the Co doped ZnSe NR(a), its Zn 2p spectra(b), Se 3d spectra(c) and Co 2p spectra(d). The typical Zn XPS is shown in figure 2(b), whose Zn 2p3/2 peak is at 1025.8 eV. The typical Se element XPS is shown in figure 2(c), whose Se 3d peak is at 54.6 eV. The signal of Co 2p shown in figure 2(d) is not good for its minor amount in the NR. Though its signal is weak, its profile is much close to the Co2+ in Co compounds, because its 2p3/2 at 780.4 eV and 2p 1/2 at 796.3 eV, both of them have respective satellite peak at higher binding energy zone (above the mainline with 4.9–9.6 eV) due to electronic correlation of the dL state [40]. This satellite band shows separate peaks in this doped system, agreeing with the theoretical prediction of separate d states population in crystal field, but seldom be seen in early cobalt(II) compounds. The satellite would disappear if Co ion becomes 3+. The Co 3s spectra reflected its peak at 103.5 eV, which is shown in figure s1 (https://stacks.iop.org/NJP/23/033019/mmedia). It is found that most of Co ions should be at 2+ state.

In order to study the optical transitions of Co doped ZnSe NRs, PL spectra of single NR have been collected. Figure 4(a) shows that PL emission spectra of different concentration of Co doped ZnSe NRs, whose corresponding Co contents are 1.07% (black curve), 0.52% (red curve) and 0.14% (blue curve), respectively. In the PL spectra of 1.07% Co-doped ZnSe NR, the first emission peak centered at 464 nm (2.68 eV) is assigned to a polaronic exciton (PX) type emission for it is close to the ZnSe bandedge at room temperature [41, 42]. The second emission band (D) at around 555 nm could not be well assigned for it has been in dispute [39, 43]. Its broadness comes from complicated physical mechanism, which would be discussed in next paragraph.

It is interesting that we are unable to identify the D emission band peak at very low Co concentration, as that for its XPS spectra. The fact reflects two cases. The first case is the forbidden d–d radiation transition rule. The lowest 4T2→2A2 d–d transition infrared luminescence of Co(II) in ZnSe is located in the far-infrared zone [44], but our emission is in the visible zone. Robbins et al [39] indicated that this is a high level d–d transition 2Γ4→4A2 (F) of Co(II) ion in ZnSe lattice at 1982. In 1982 they [45] studied their magnetoluminescences and uniaxial stress transitions, and indicated that it came from the high level L, M, N absorption lines of Co(II) ion in ZnSe, and the transition of L line and its satellite might be from d states to conduction band, and vice versa for the PL, in which the spin–orbit and spin–spin interactions should
be included, moreover, its excited state is weakly related to Co(III) configuration, with a vibronic profile. However, Dreyhsig and Litzenburger [43] indicated the above mentioned L, M, N absorption lines should be the internal transition of Co ions, but possibly a multiplet state via the ligand-field and charge transfer processes, that may be favored by the spin–spin interaction. Yumashev et al [38] indicated that visible emission of Co ions in oxide could be also realized by the nonlinear optical excitation or even absorption, just as that the nonlinear optical absorption phenomena or pair excitation in ZnSe:Co$^{2+}$ crystal. In our previous publication, it is known that the high level d–d radiation transition in this zone could happen due to FM coupling between neighboring Co ions in Co pair or cluster in a DMS [14]. The TM ion clustering is one origin of the ferromagnetism and pair excitation in DMS [46]. For low concentration, there is no neighbored Co pairs, and single Co ion in doped ZnSe NRs cannot produce their radiation transition, but a little higher concentration Co ions can be FM coupled and give their broad emission band. The second possibility is the existence of a p-type hole due to deficient Se. The hole may transform its neighbor Co(II) to Co(III), though few, and Co(III) has a higher energy than Co(II), that near the ZnSe band-edge rather than that in the local crystal field region. Co(III) occurrence could cause high p–d hybridization and John-Teller effect at the same time [47], as well as the ferrimagnetism. Such state and related defects can modify their spin states and reduce the radiation transition for d–d transition, often minor for the less Se deficient and EMP formation case.

Actually the CVD growth of ZnSe crystal often form Wurtzite–zincblende polytypism [48], and doping TM ions may also cause John-Teller effect related structural instability [47]. Moreover the stacking faults effect on the visible emission of Co(II) ions have been identified in ZnS:Co crystal [32, 49]. Figure 3 give the XRD pattern of the Co doped ZnSe NRs (both zincblende and WZ phase crystal cards presented), in which the zincblende structure pattern has been identified with dominant intensities, however, a lot of very small peaks labeled in figure 3 show up at the WZ ZnSe crystal [101], [102], [110], [112], [210], [300], [302] patterns, which indicates that the stacking fault layers connected Zincblende–Wurtzite–polytypism forms in such CVD grown NRs. From this doped NR, the two phases, defects and varied magnetic polaronic states may take action simultaneously. The TEM morphology of as prepared ZnSe:Co nanowire and belt with more stack fault layers have been shown in figure s2. Even though no clear morphology character in the nanobelts or nanowires, the Raman spectra for doped and undoped ZnSe NR under 532 nm laser excitation with varied powers still can give clear paired acoustic phonon modes as shown in figure s3, which unusually reflected their stacking fault layers related acoustic phonon modes at 144 cm$^{-1}$ (2TA(L)), 186 cm$^{-1}$
(2TA(X)) and 312 cm\(^{-1}\) (2LA) in the pure lattice. Moreover, after Co doping it is found that the LO phonon mode at 256.5 cm\(^{-1}\) prevail over the TO mode at 208.5 cm\(^{-1}\) in doped ZnSe, together with dominance of the 4TA(L) mode at 294.7 cm\(^{-1}\), and clear 2LO phonon mode at about 500 cm\(^{-1}\), that all reflected significant enhancement of electron-phonon coupling in Co doped ZnSe NR, out of the structural relaxation and deformation potential by Co incorporation. With increasing Co(II) doping, the Co–Co coupling also increases, resulting in possible Co ion pair formation and high level d–d emission [14], then the emission peak becomes dominant with rising Co ions, as shown in figure 2(a), though even lower d–d transition exist, they are out of my detection range [50]. This phenomenon could also be observed in Co doped CdS belt [14]. The doped FM aggregated TM ions in semiconductor by CVD growth environment can happen easily at its circumventing temperature [11], depend on no material types [46]. Therefore the intrashell high-level d–d radiation transition occurs in these transition metal (TM) ion doped DMS NRs. Moreover, the FM coupled TM ion pair could also produce the nonlinear optical absorption by local pair excitations in complicated oxide nanocrystals, whose lifetime could be lengthened by the charge-transfer band involvement [51].
The intensity ratio of band-edge emission (X) and Co$^{2+}$ d–d transition emission (D) varies with Co ion content in NR, which seriously affects the visual color of the NR emission. Figure 4(b) shows the emission color change in Co doped ZnSe NRs due to the different intensity ratio of two PL emission bands. The wavelength of X emission is 462 nm with a blue color, while Co$^{2+}$-related d–d transition emission (D) occurs at about 550 nm with yellow–green color. So their mixed color for the whole NR emission covers blue, green, yellow, and even white at room temperature if their relative intensities vary, which are marked in the red ellipse area of the International Commission on Illumination (CIE) coordinate in figure 4(b). Furthermore, temperature change can also modify its emission color. With decreasing temperature from 300 K to 77 K, the emission color gradually changes to green along the red arrow direction, as shown in figure 4(b). Therefore, close to monochromatic light, such as blue and yellow light can be obtained only by combination of band-edge exciton emission and D emission of Co ions in ZnSe lattice, while the mixed white light can also be seen by the varying Co content and emission peak intensity ratio in Co doped ZnSe NR.

The absorption spectra and luminescence spectra of Co$^{2+}$ d–d transition in ZnSe bulk material have been reported in many publications [43, 52–54], especially in the high d level excited state of Co$^{2+}$ in visible range. In Co doped ZnSe nanocrystals the magnetism have been identified though hard Co ion incorporation in the core of nanocrystals [55]. The bandedge emission enhancement by minor but not heavy Co(II) ions incorporation in varied nanocrystals have been observed [56, 57] undoubtly due to FM spin–spin and spin–lattice interactions, that is found much stronger in the bulk [36]. In Co doped ZnSe NRs, more Co$^{2+}$ ions would approach each other in the lattice for the higher growth temperature than the doped QDs in solution, the Co FM couplings would become even popular in the crystal formed in CVD technique, which could result in the emissions out of their high d level excited states due to the radiation relaxation of d–d transition rule of Co$^{2+}$. This optical transition is often called ‘intrashell emission’ because it is not the lowest d–d transition [58]. Such a FM enhanced effect on high level d–d emission often exists in DMS with nonlinear optical effect [4, 14, 15], and changes their d state lifetimes of the doped TM ions as well as the induced exciton lifetime near band-edge due to the EMP and LEMP formation.

The real-color images of the NR emission are shown in figures 5(a) and 5(c). Figure 5(a) shows power-dependent real-color image of single NR excited by 405 nm laser in the dark field. It is observed that as the excited power increases from 0.2 mW to 17 mW, the NR becomes brighter and its corresponding emission color is dominantly yellow. Corresponding power dependent PL emission spectra of this NR at room temperature is shown in figure 5(b). The X peak near band-edge shows a slight red-shift with power increasing which is due to the fact that the carrier density increases in NR by CW laser excitation and the bandgap renormalization happens based on the carrier thermalization with increasing power [59].

Emission band D has also been studied by varying excitation powers. The intensity of D emission band was also enhanced significantly with power increasing, which is in contrast to the minor reduction of normal deeptrap emission by defects, and the D peak position has almost no shift due to its d state localization nature. Both emission bands of this NR can become stronger and brighter at the same time at higher power excitation, so its emission color has no obvious variation but brighter, which have been shown in figure 5(a). This D band is very broad because it contains a lot of different d levels and nonlinear
interactions, for example, exciton–phonon, exciton–spin, spin–spin, spin–carrier and spin–phonon couplings, which can expand their energy range naturally. Such behavior also could be seen in the CdS:Ni NRs [15], which even give dual lasing lines at high fs pulse pump. Based upon this lasing phenomenon, it is known that fs pulse can excite these excitations resonantly with more coherent way and produce limited or separated interactions within the excited states.

The NR emission color can vary at different temperatures as shown in figure 5(c). At 77 K, the dominant color is green but become yellow at 300 K, which is the superposition effect produced by the redshift of both of the two emission band when temperature increases from 77 K to 300 K. With the increasing temperature, the intensities of X emission near band-edge decrease and the X peak red-shifts, as shown in figure 5(d). These characters reflects the exciton–LO phonon coupling [60, 61] with an additional EMP formation [14]. In figure 5(d) the D emission band also has a slight temperature dependent redshift with rising temperatures, which reflects the D band is not completely the d–d transition, possibly with some defect or chemical bonds involved d state because the d–d transition is usually not shifted with temperatures. If it contains only d–d transition of Co ions, such emission band could only be from the high level d–d transition out of FM coupling Co pairs as indicated above, but not single ion, because the pair Co ion cluster needs some p–d hybridization. In current situation this d state forms LEMP, not a fully intrashell local d state, but with clear spin-orbital interaction by the p–d hybridization [17]. Both the EMP and LEMP form with the contributions of LO phonon coupling with exciton [13]. This is common in TM ion doped II–VI and III–V dilute magnetic semiconductor [62, 63]. Moreover, the intensity of D emission peak goes down fast with increased temperatures, strongly indicating that this LEMP has relations to the structural defects in this doped ZnSe NR.

Furthermore, the PL lifetime measurements for the same single NR have been carried out using a pulse laser at 405 nm. Figure 6(a) shows the lifetime data of X near band-edge emission at room temperature. The blue hollow circles are the experimental data and the red solid line is the fitted curve based on single exponential function $I(t) = I_0 + A \exp(-t/t_0)/\tau$ with the fit lifetime $\tau$ of 0.813 ns, which is a little longer than that reported in pure ZnSeNR [64] due to the EMP formation. Figure 6(b) shows the lifetimes of X near band-edge emission with temperature variation. At different temperatures, the lifetimes have a little fluctuation, that may be some interactions with structural relaxation in this system. Figures 6(c) and (d) show the lifetime decay for the D emission band at room temperature and low temperatures. In figure 6(d), there occurred clearly two components at low temperature, an obvious short component (1.98 ns) and a longer lifetime component (300 ns), to be discussed in next section.

Figure 5. (a) The real-color images of the NR emission at different excited power in the dark field of microscope. (b) PL spectra of the NR in (a) with excited power increasing. (c) The real-color images of the NR emission at different temperature in the dark field of microscope. (d) PL spectra of the NR in (c) with temperature changing.
Figure 6. Normalized PL lifetime decay curves of an individual Co-doped ZnSe NR. (a) Normalized PL lifetime experimental measurement curve (blue hollow circles) and its fitted curve (red solid line) of X near bandedge emission at room temperature. (b) Normalized PL lifetime experimental measurement curves of X near bandedge emission at different temperatures. (c) Normalized PL lifetime experimental measurement curve (blue hollow circles) and its fitted curve (red solid line) of D emission (Co$^{2+}$ d–d transition emission) at room temperature. (d) PL lifetime experimental measurement curves of D emission at different temperatures. The blue hollow circles are the data of experimental measurement and red solid lines are their fitted curves with single-exponential decay function shown in (a) and (c). The data are obtained by a pulse laser with exciting wavelength 405 nm and excitation density 230 μW cm$^{-2}$.

The D state works as indicated in above section has some possibilities for its origin: (1) surface state; (2) point defect or structure defect; (3) impurity defects (Co ion doping). Surface state can be weakened by passivating the surface [65]. Zn vacancy and stack fault defects have also been thought to be common point defect [66] and structure defect in ZnSe, whose shape of the emission band and FWHMs vary largely with increasing temperature [65, 66]. These three states must have very similar energy value, to match with our emission lifetime experimental results. Therefore, to further understand its origin, the lifetime analysis has been carried out. Figure 4(c) shows the D emission peak lifetime at room temperature fitted by two exponential function $I(t) = I_0 + A \exp((-t - t_0)/\tau)$ with the short and long lifetime $\tau$ of 2 ns and 300 ns respectively, the short term should be the LEMP component; the longer over 200 ns may be the emission out of possible Zn vacancies proposed by Xing [64]. In our NR, Co + Zn is excessive, so no Zn vacancies. Simple point defect or structural defect with charges has no so long lifetime emission. This indicates that there is another origin for a long lifetime component in the D emission band. Figure 4(d) shows lifetimes decays of D emission band at reducing temperatures. At temperatures <300 K, anomalously sudden-rising lifetime enhancement in the intermediate state has been detected, in which two lifetime components at varied initial time could be obtained at low temperature. This situation happens usually in a system that there exist two potential minima (quantum well) at the varied atomic coordinate locations with equal energy out of two structural or composition co-existing phases as shown in figures 7(a) and (b). In this doped semiconductor, there occurs another incorporated potential valley (PV, green curve) near the intrinsic atomic potential well (Γ$^a$). There is an energy barrier ($E_{ph}$) between Γ$^a$ and PV energy level and this $E_{ph}$ is close to the thermal energy $kT$ (26 meV) at room temperature. At high temperature $\geq$300 K, this potential barrier disappears and two potential wells may be mixed, so there is no obvious process of lifetime secondary rise and decay as shown figure 6(c) and the dark-blue curve in figure 6(d). But at lower temperature $T$, the barrier may become higher than $kT$, the tunneling could happen due to the close spatial distance between two phases, for WZ and ZB phases in this NR, so their secondary lifetime could accompany to form separately. This similar phenomenon is much like that happened in aged porous silicon, a composite silicon nanocluster capped with a shell of SiO$_x$ [67, 68]. In figure 7(a), the blue line state is originated from the dopants, while the green line state comes from the intrinsic defects. So the D transition between high $d$ excited states and ground state of Co$^{2+}$ ion could be mixed with a selftraped exciton out of the stacking fault defect trapped states of a long lifetimes. From the XRD pattern in figure 3 this structural defect could be at most assigned to the minor wurtzite phases or the stacking fault layer between the WZ–ZB interfaces. Hence the potential valley out of stacking faults or the two phase interfaces would
Figure 7. (a) Schematic of recombination dynamics of excitons ($X$), EMP or BMP near bandedge and high d excited state to ground state of d–d transition of $\text{Co}^{2+}$ ion (blue color) and STE (green color) within bandgap of Co(II) doped ZnSe NR. (b) The electron level potential diagram with atomic coordinates in Co doped ZnSe NR.

confine Co ion aggregates in NR, which could lead to one enhanced ‘intrashell transition’ [14, 58], overlapped with the coexisted selftrapped exciton (STE). The combined state of FM coupled d–d transition of Co ions and STE would lead to the accumulation of photo-excited electronic states in the potential valley with pair excitation, that is why a strongly enhanced green colored emission rises with powers, because it contains a very long lifetime component. Concerning this structural defect involved optical process, we can also see its existence due to the stacking fault defects in this CVD grown NRs or NWs, as shown in figures S2 and S3.

After discussion on the Co-related deep level D emission, the $X$ near band-edge emission of an individual Co-doped ZnSe NR has also been studied at room temperature by a fs pulse laser pumping at 405 nm with 150 fs duration time and 1 kHz repetition frequency. Figure 8(a) shows the optical image of single NR in the bright field of microscope when a pulse of fs laser pumps on one NR, it produces a bright emission spot at the excitation location. The emission spectra of an individual NR at fs pulse excitation often produce emission near the bandedge due to the FX and/or the magnetic polaron related bound exciton. Their emission profiles with increasing pump power from 15 μW to 40 μW were shown in figure 8(b). When the pump power is 15 μW, the FWHM of the emission peak is large and its intensity is very weak. With the increasing pump power beyond the threshold value of 20 μW, its intensity becomes enlarged at ten times, and shows an obvious emission amplification behavior and sharp FWHM reduction, as shown in the inset of figure 8(b). The FWHM and intensity of emission band vs pump powers have been summarized in figure 8(c). It is found that the FWHM sharply decreases from 12 nm to 2 nm for just over the threshold, and thereafter it has a little increment with further increasing pump power after 30 μW. This FWHM variation phenomenon in this high power range is different from traditional lasing behavior such as exciton or EMP lasing, whose FWHMs are usually monotonous decreasing with rising powers [14]. At the same time, their intensities still keep increasing rapidly and show a superlinear behavior with increasing pump power as shown in figure 8(c), like that in the traditional lasing by exciton scattering. In contrasting to the case for EMP lasing of no line-shift with rising powers [14], figure 8(d) shows a anomalous blue-shift of emission energy with increasing pump power. The spontaneous wide emission band maximum is at about 465 nm at 15 μW pump power. It produces a 468 nm lasing line at 20 μW excitation. With further increasing pump power, the lasing line shifts clearly from 468 nm to 464 nm. This is a surprising large shift for lasing line. If the photo-induced electron–hole plasma dominates in its high excitation lasing, the lasing line should redshift [69]. For intrinsic exciton phase in bulk, their lasing line can have a very small blueshift at about several meV at most, which is due to the exciton scattering in 3D space. So the above clear blueshift of lasing lines should be due to the strong scattering between excitons in a lower dimensional structure, for example 2d structure. Amand et al [70] indicate that an enhanced blue shift and splitting of exciton emission line could happen in spin polarized dense excitons in quantum wells. This conclusion proposes two characters from our system to account for the lasing and emission processes. One is a QW structure form in this doped NR, that is easy, the stacking fault layer between WZ and BZ zones can form QW to trap Co ions. Another is that BMP contribute to this lasing line shift, because only the local BMPs can have so
strong coulomb repulsion scattering, with both LO and TA phonon involved in the electron–phonon coupling, together at the electron–electron interactions in the exciton phase.

Based upon the above discussion, we know, there are coupled Co(II) ions in the normal and defects in NR, that may cause the EMP and BMP, which is described in detail as follows. Besides such situation, some of Co dopants can stay with fixed defects and local charges, i.e., minor Co$^{2+}$ ions may transform into Co$^{3+}$ with John T ell instability at excited state, then the excited bound EMP would undergo the AFM coupling between Co(II) and Co(III) and transform into BMP [19], in which strong electron-correlation in AFM state between Co$^{2+}$ and Co$^{3+}$ would dominate in the local potential valley or defects. Yang et al [71], reported the Zn interstitial in defects may modify the Co AFM coupling to FM behavior with high stability in Co doped ZnSe crystal, which supported the defect-facilitated BMP formation in their optical and magnetic experimental results [19]. Hence its strong Coulomb repulsion in a confined BMP nanosystem or a defect structure would exhibit in this spin-polarized exciton and their scattering at high excitation, hence produce large blueshift and broadening lasing [72]. The co-existence of lattice defects and TM dopants could lead to form EMP or BMP in the QW out of regular defects. These magnetic polarons in such local structure possess stronger coulomb and exchange interactions, lead to stronger nonlinear optical effect than the situation without MP. For example, a new excited absorption [37] by bie exciton [51] for coherent absorption and an emission out of above mentioned long lifetime magnetic polarons in their respective spectral range could happen. Therefore a higher MP exciton binding energy and attracting force between magnetic excitons in the coherent excited states produce the above mentioned lasing behavior in some DMS system as that in TM FM oxides [51].

According to the above phenomena and physical background, it is known that there are different magnetic excitons near band-edge for different TM doped semiconductors, whose optical behavior may exhibit varied profiles with excitation power. At low excitation power, the $X$ for perfect DMS crystal should be mainly EMP ($L \rightarrow d_{nL}$). In this exciton density zone, the Co–Co FM coupling contributes to EMP formation. The as formed EMPs can form collective EMPs near band-edge at high excitation, an EMP condensate for bosonic lasing [14] in semiconducting structure even without clear optical cavity. Mietki and Matuszewski [27] indicate that this EMP condensate may be an exciton polariton condensate due to the selftrapped magnetic polaron but like that exciton in the cavity. In our observation, the EMP may form at initial fs excitation, probably not for BMP because of its 2d nature, with no superfluidity or yes. Their exciton phase diagram deserves more study experimentally. However, for the electron or hole doped DMS structures, the even localized BMP or bound carriers may be more significant in their optical responses near

![Figure 8](image)

**Figure 8.** (a) The optical image of an individual Co doped ZnSe with fs pulse laser pumping under the microscope. (b) Pump power dependent emission spectra of the NR with wavelength 405 nm and pump power from 15 W to 40 W of fs pulse laser. The intensity of emission spectrum of pump power at 15 $\mu$W enlarges ten times. Inset shows emission spectra of pump power at 15 $\mu$W and 20 $\mu$W, respectively. (c) FWHM (black dotted line) and intensity (red dotted line) of emission spectra of NR variation with pump increasing power. (d) The shift of emission peak position with pump power increasing.
the bandedge in real DMS, because defect or vacancy related carriers almost cannot be avoided in various preparation process. The BMP often stays in a local zone where there are charge or structural defects or potential well in its structure, which is almost no temperature-dependent relationship but only related to the local carrier density population \[19\]. This BMP is an interesting phenomenon, the usually formed AFM pair involved in such relaxed structure can cause the mutual cancellation for their deformation related electron–phonon coupling out of single TM ion in lattice. Moreover in AFM system the d state often have strong electron–electron correlation effect on the exciton energy and bandedge magnitude. Therefore the BMP population often come with strong coulomb repulsion as that spin-polarized excitons in low dimensional structure \[70\]. When excitation is over 20 \(\mu\)W in our system, more excitations would go down to EMP, and minor bound magnetic exciton trapped by the defects, for example, the stacking fault layer in this ZnSe NR. Its carriers are of highly d component with high electron–electron correlation and high binding energy for pair excitons. Over this EMP excitation, the equal energy BMP would be highly populated later. At such a situation, the d–d electron correlation would be accompanied by their magnetic PX scattering and significant blueshifted lasing lines with powers, but not traditional electron–hole plasma by s, p electrons in semiconductor. Moreover, this clear blueshift of lasing line come also with a clear band broadening, due to the enhanced exchange interactions in high density MP interactions for the EMP and BMP co-existence.

We have calculated the band structures of Co doped ZnSe crystals by the VASP software as shown in figures S4(A) and S4(B). The chemical stoichiometry is good for this zinc-blende system. The high Co amount in the doped ZnSe NR represent that there are FM coupled Co ion pairs and possible (AFM) coupled pairs inside the lattice. Both calculated bandgap values of two doping situation with standard lattice parameters are underestimated as compared to the intrinsic bandgap values, that is normal for this DFT calculation. Though the absolute and quantitative parameters may not be very good, but the comparison for their relative data is meaningful for this calculation. From the calculated results the bandedge for ZnSe lattice with the AFM coupled Co ion pair becomes larger, due to its d–d electron–electron correlation effect and cancelled electron–phonon coupling, than that with the undoped and FM Co ion pair (spin up case), this conclusion is convincing. For the spin-down case, the d–d transitions have been enhanced and its transition exhibits redshift. This is in good agreement with our experimental results. The above calculation results prove that the FM pair stays in the normal lattice, determining their basic DMS properties. If the studied NR with AFM doping shows bandedge emission peak (green line in figure 7(b)) very close to the similar energy of EMP (blue line in figure 7(b)) in FM Co pair, the AFM pair should favor to stay in the stacking fault defects (BMP), as suggested by the experimental results in ZnSe:Mn NB \[17\], and calculated results on ZnSe:Co(II) by Yang et al \[71\]. The EMP lifetime in DMS nanostructure is usually within about 2 ns if no structural defects \[11\], slightly longer than that of FX. Our measured lifetime for this MP emission in figure 6(b) is 0.813 ns, which is smaller than that of EMP, proving that there is MP competitors nearby. So our bandedge emission here should not be the usual EMP at initial. They may contain some BMP or a composite of BMP and EMP. The short lifetime may be due to the fast exchange between EMP and BMP at the same or close energy.

The magnetic properties of ZnSe:Co NRs have been obtained as shown in figure s5. In the magnetic hysteresis curves at 2 K and 300 K, we can see the ferromagnetism in this sample, and the low temperature results indicate there is some paramagnetic responses. The irregular hysteresis curves reflected the complicated magnetic coupling in the sample \[11, 15, 19\]. The magnetic susceptibility curves versus temperature at 1000 Oe and 5 Oe reflected the Curie temperature for this sample is larger than 300 K. The former shows a magnetic response increment in the 75–300 K zone, while the latter show a similar profile in the 50–300 K. The latter curve represents the zero field response because the magnetic field 5 Oe is used to compensate for the negative remnant magnetic response for the sample container and facility. The ferromagnetism is indeed present in this ZnSe:Co NR even at room temperature.

Why the above behavior happens, the Co ions in stacking fault layer have been found to show a d–d transition splitting \[73\], which is dependent on the micro-environments of Co ions in varied crystal fields and local interactions. Due to the multi-level of Co ion in the relaxed lattice and Co–Co spin coupling, some of the local d–d transition in the vicinity of 550 nm at LEMP would combine with LO phonons to behaves like a STEs with longer lifetime, as shown in the multi-lifetimes at low temperature in figure 6(d). This relaxation-rise- relaxation phenomenon is also the typical evidence for the structural relaxation involved exciton state and re-relaxation in this NR.

The band minima connected with the coupled d band in figure S4(A) indicate that two states of LEMP-d states and Zn 4s state in defects may cross each other at some coordinate x value to form the bound state so the suddenly increased lifetimes could be seen in figure 6(d). For both of the Co doped ZnSe lattices the ground state all composed \(\varepsilon_g\) states of Co d orbitals near the Fermi level, the electron-correlation with large correlation energy U dominate at the excited states with narrow DOS, which therefore cause the high
Figure 9. The microscopic interactions and excitations in a DMS structures with varied doping concentration and relaxed structures (the red arrow represent the energy magnitude). The red arrow indicates the direction of doping contents in the lattice.

blueshift due to the enhanced U in the DMS structure. In early literatures, the coexistence of AFM and FM structure in a pure substance has been seen only in some layer compounds like MX$_2$ (X = F, Cl, Br and I, M = transition metal ion) [74], now their coexistence observed in this DMS indicates the existence of layered Co ions in the stacking fault defects between two phases in NR [15, 75]. The re-lifting of polaronic d–d transition emission lifetimes at low temperature in figure 6(d) reflected the coexistence of two above magnetic states, which is also accompanied with the increased ferromagnetism in this DMS structure. Such FM coupled situation should be in agreement with the above spectral profiles and previous nonlinear optical properties.

Until now there are reported lots of magnetic semiconductors from different origins in wide bandgap semiconductors with varied dopants [76–79]. Their ferromagnetisms come from various local interactions, including the spins from TM ions, carriers or vacancy or surface relaxation. What we discussed here is that the TM doped semiconductor, in which the substitutial TM ions have the same valence with cationic metal ion in semiconductor matrix. We try to find the conditions to realize the EMP for their collective condensate for bosonic lasing, the EMP needs the FM coupling TM pair or clusters in the same local symmetry as the semiconductor itself, but not the natural local symmetry in its TM compound. As in nonmagnetic ion doped magnetic semiconductor [78, 79] whose elementary excitation and optical properties still need study in the future.

The local ion distribution and structural profile could cause different interactions for a non-uniform TM doped semiconductors as shown in figure S6. These interactions could be exhibited in their excited states after photo-excitation, especially in their PL spectra. That is to say, the EMP and BMP could coexist in a definite zone for a same DMS as shown in the overlapped zones in figure 9, proposed from a lot of sparsely or randomly doped semiconductors at optical excitation. In such a system under excitation above bandgap the EMP could dominate in an ideal substitutial doping structure [14, 15] but some BMPs could exist in a relaxed structure or with defects or interstitial case [77]. At first the EMP has higher stability due to coupling to LO phonons and coupled spins, hence often possess lower energy than BMP so its PL occurs at low excitation power. If encounter the defects or charged vacancy, BMP may form with localized nature or low dimensional zone. Its high population would act with a confined structure. It is very interesting that the electron correlation by d electron narrow band and spin coupling between TM ions play important roles in PL spectra, but the electron–hole plasma in s–p bond semiconductor cannot be produced at low doping and dominate its high excitation optical behavior, for example, the sp bond semiconductor usually exhibit the band-filling effect due to optical bleaching (negative absorption) at high excitation. Hence this Co doped ZnSe crystal exhibit strong positive nonlinear absorption near bandedge due to magnetic polaron [33], like a biexciton absorption, whether what magnetic polaron exist. Accompanied with this biexcitonic-like state absorption character, lasing behavior by pulse excitation could be used to verify their exciton interaction characters and tune their responses in DMS, because their composition, structure,
microscopic interactions, excited state and collective effect are combined to form different MP states to contribute to emission and lasing, the excited excitonic phases formed in different composition products by varied preparation techniques can be shown in figure 9. With increasing dopants, the carrier effects become more significant, and excitonic effect may be reduced for efficient PL and lasing. Definite doping below a critical dopant concentration is important for their optical responses.

In fact the study on the optics of DMS can unveil more MP characters in these DMS structures, which combine both Wannier and Frenkel exciton nature with strong spin coupling profile, could lift their understanding and applications. Moreover, the lasing process in this structure, easily trigger the exciton condensation via spin coupling, or spin-exciton polariton [27, 29], which may have more applications in the future quantum technologies, especially the spin polarized bosonic lasing from collective EMPs and BMPs. Therefore, preparation the material or structure with more MP profiles and understanding their microscopic interactions and optical responses are very important in the spin-related photonics.

4. Conclusion

We successfully synthesized uniform distribution high quality cobalt doped ZnSe NRs by the CVD method with the dilute magnetic nature. There are two PL emission peaks from an individual Co-doped ZnSe NR in the visible region: magnetic exciton emission near bandedge and high excited d level transition emission of Co²⁺ within the gap. Their relative intensities and emission color could be modulated by changing the concentration of Co ions. The aggregation of Co ions fall into the potential valleys out of the defects (Γ₄) or QWs between ZB and WZ phases to form the LEMP, results in long d–d transition PL lifetime and very bright luminescence. This LEMP is composed by the overlapped states of the excited d state and L, M, N d multiplet. When temperature lower than 300 K, anomalous lifetime enhancement of LEMP in an intermediate state have been detected for enhanced ferromagnetism at low temperature, in which there are two components of lifetimes, represented the co-existence of both magnetic polaron and PXs. At room temperature, the high level d–d transition of coupled Co²⁺ ions and defect potential valley transition merge and give long PL lifetime of 292 ns, which also be indicative of ferromagnetism origin by emission.

The fs laser pulse pumps on an individual Co-doped ZnSe NR produce obvious EMP lasing behavior at the threshold. However, its lasing line shows blueshifts and broadening with rising powers, indicating a crossover from EMP to BMP or charged EMP in Co doped ZnSe NR during fs excitation, with a positive nonlinear absorption out of transient biexciton due to the Co ion FM coupling induced attraction. This BMP lasing may possess local nature with strong coulomb repulsion or in a QW defect in the NR. These findings indicate the complicated ferromagnetism and structural inhomogeneity, coexisting magnetic polarons and relaxed structure, as well as anomalous optical properties in Co doped ZnSe NR, which can be partially verified in reference [71]. Such TM doped magnetic semiconductor nanostructures may have potential applications not only in the lighting, display, laser and other optoelectronic devices, but also on spin-related nanophotonic devices.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Conflict of interest

The authors declare no interest conflicts.

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