# EMP Formation in the Co(Ⅱ) Doped ZnTe Nanowires

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*Co(Ⅱ) doped ZnTe nanowires are prepared by a thermal evaporation method. The power and temperature dependent micro-photoluminescence spectra of single nanowire demonstrate the double bands near its band edge, and the ferromagnetism behavior for these nanowires is identified. The occurrence of excitonic magnetic polaron (EMP) can account for the second emission band for its higher binding energy and ferromagnetic coupling. This EMP formation in a nanostructure will facilitate to realize magnetic modulation on confined excitons and will find new applications for spinpolarized nanophotonic devices.*

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Transition metal ion doping in semiconductors can modify the electrical, optical and magnetic properties of semiconductors, bring about the field of diluted magnetic semiconductor,[1,2] in which the excitonic magnetic polaron (EMP) as a new excitation of exciton combination with ferromagnetic coupled spins was identified.[3,4] Our group observed the formation of EMP in a series of TM (transition metal) doped wide-bandgap diluted magnetic semiconductors (DMS) microstructures: Mn doped ZnO,[5] ZnSe[6,7] and $CH_3NH_3PbBr_3$.[8] In addition, we also found that CdS:Co and ZnO:Mn NWs could be excellent candidates for the observation of bosonic lasing due to the coherent radiative transition of collective EMP.[5,9] These Ⅱ–Ⅵ semiconductors, which have the common characteristics of wide bandgap $E_g$ and high exciton binding energies, are easy to form independent EMPs with exciton-spin interactions if their size is over a micrometer EMP which is a type of bound exciton, i.e., spin-polarized magnetic exciton, which could be controlled by the outside magnetic field to initiate more applications.

Zinc telluride (ZnTe) belongs to the compound of which the bandgap is approximately 2.28 eV (∼545 nm) at room temperature and the exciton binding energy is approximately 12.6 meV,[10,11] in which its free exciton could not be observed at room temperature. Ⅱ–Ⅵ semiconductors are demonstrated potential properties and widely used in lasers[12] and photodetectors.[13] ZnTe is an attractive material for various optoelectronic devices, such as green LEDs, nanosensors and photovoltaic cells.[14,15] The exciton binding energy of ZnTe (12.6 meV) has an intermediate magnitude in Ⅱ–Ⅵ semiconductors. The cobalt ion has a $3d^7$ electron configuration and could substitute the cations in Ⅱ–Ⅵ semiconductors. In the early report by Arfan *et al.*, the Mn and Ni doping in ZnTe nanobelts were found to shift their band-edge emission with increasing the excitation due to the enhanced electron-phonon coupling, strong electron-electron correlation and carrier scattering, but with no EMP profile. This indicated a difficulty in the formation of EMP in TM doped ZnTe due to their low exciton binding energy. In this work, we prepare Co-doped ZnTe nanowires with the chemical vapor deposition (CVD) method and investigate the power and temperature dependent emissions by micro-photoluminescence (PL) of nanowires. It is surprising that a clear indication of EMP profile is identified in the single wire μ-PL detection.

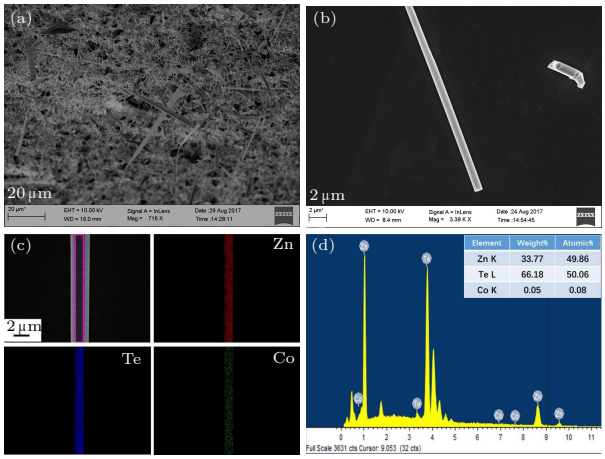


**Fig. 1.** (a) Low-magnification scanning electron microscopy (SEM) image of as-prepared Co-doped ZnTe nanowires. (b) High magnification SEM image of an individual Co-doped ZnTe nanowire. (c) Energy dispersive spectroscopy (EDS) elemental mapping of three elements Zn, Te, and Co, respectively. (d) EDS profile of an area of Co-doped ZnTe nanowire of (c).

The nanowires obtained by the CVD method are discussed in the supporting information. The morphology of as-prepared Co-doped ZnTe nanowires is shown in Fig. 1(a). Figure 1(b) shows a high magni-

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fication SEM image of an individual Co-doped ZnTe nanowire which demonstrates that the surface of the nanowire is clean and smooth. Figure 1(c) shows the high-magnification FESEM image of a nanowire and the rectangular box indicates the selected area for EDS mapping. The elemental composition of Co-doped nanowire is shown in EDS in Fig. 1(d). Figures 1(c) and 1(d) confirm the presence of three elements Zn, Te and Co, illustrating that Co ions are successfully doped into ZnTe nanowires almost uniformly with a Co atomic percent of about 0.08%, and the stoichiometric ratio of zinc and tellurium is close to 1:1.

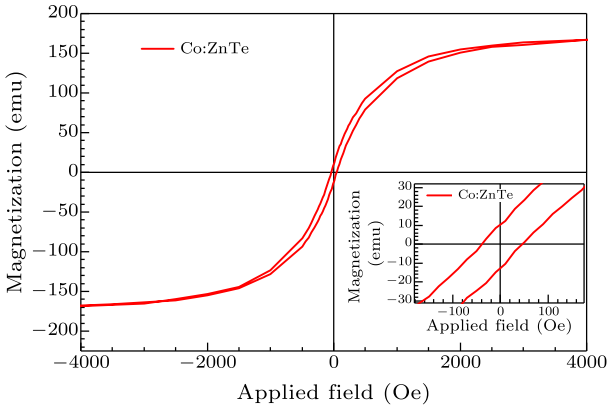


**Fig. 2.** The $M$–$H$ curves of Co-doped ZnTe nanowires measured by SQUID at room temperature. Inset: the magnified area near zero magnetic field of $M$–$H$ curves in the vial.

Figure 2 shows the magnetization of Co-doped ZnTe nanowires as a function of the applied magnified field ranging from −4000 to 4000 Oe. The inset is the magnified area of the corresponding $M$–$H$ loop. A good magnetic hysteresis loop is shown in the $M$–$H$ curves ±4000 Oe, indicating the ferromagnetic behavior of Co-doped ZnTe nanowires.

The μ-PL spectra of a pure ZnTe nanowire excited by cw 405 nm laser at 80 K is obtained in Fig. 3(a), which shows that the near band-edge emission peak at 545 nm at 80 K can be assigned to the free exciton (FX) emission band, which has a symmetric profile near the band-edge. Figure 3(b) shows the PL spectra of ZnTe:Co nanowire at 80 K. The inset is the fitted PL bands for the band-edge emission, whose spectral profile could be well fitted with the Lorentz functions. The shoulder (550 nm) at the long wavelength side of the mainline (546 nm) of emission band shows up, which is different from the pure ZnTe nanowire. The peak fitted for the shoulder is located at 549.68 nm with a separation to mainline (FX) of 19.4 meV. This span energy (19.4 meV) is less than the largest LO phonon energy (26 meV) of ZnTe. Hence, this emission peak may be assigned to excitonic magnetic polaron (EMP) instead of LO phonon replicas.[16] Aggregate of Co ions can possess ferromagnetic spins, which can bind with FX to form EMP, which give emission as a shoulder. At the same time, a broad emission band range from 600 nm to 900 nm can also be observed, which are the $d$–$d$ radiative transition $^4T_1(P) \rightarrow {}^4A_2(F)$ next to the band-edge emission due to ferromagnetically coupled Co ions in the lattice.[9,17] This $d$–$d$ transition in the visible range occurs from a high $d$ level but not the lowest $d$ excited level. This phenomenon is called the 'intrashell emission' for $d$ state.[18] Moreover, its occurrence proves the aggregation of Co ions in the ZnTe lattice.

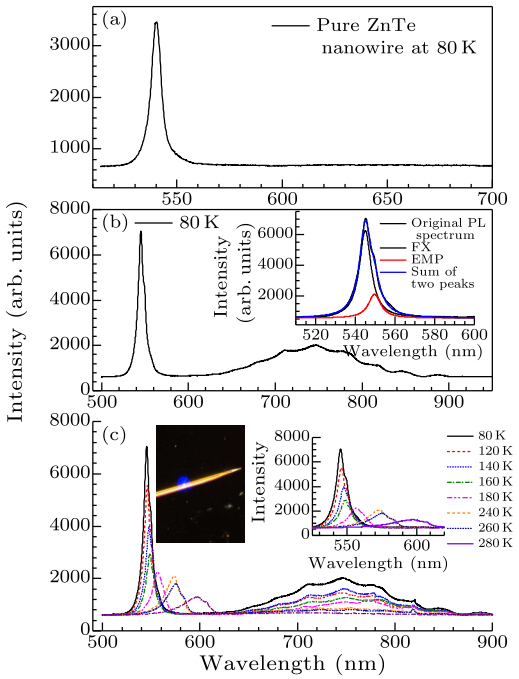


**Fig. 3.** Temperature dependence PL spectra of a prepared nanowire under 405 nm cw laser excitation. (a) The PL spectra of pure ZnTe nanowire at 80 K. (b) The PL spectra of ZnTe:Co nanowire at 80 K. The inset is the fitted PL spectra of the band-edge emission (composed of FX and EMP) with the Lorentz function. The black curve is the original PL spectrum, the red and green curves are the fitting spectra of the Lorentz function curves, which represent FX and EMP, respectively. The blue curve is the sum of two curves. (c) PL spectra of the ZnTe:Co nanowire from 80 K to 300 K. The insets are the corresponding optical image and luminescence spectra from 500 nm to 660 nm at different temperatures, respectively.

As shown in Fig. 4(a), it has been obtained with the fitted PL spectra (520630 nm) of the emission with Lorentz function at excitation power $P = 2.98$ mW. The black curve is the original PL spectrum, the Lorentz Function curve (LFC) 1 and LFC2 are fitting curves of the Lorentz function, and the blue curve is the sum of them. In this spectrum, there are two emission peaks at 564 nm and 573 nm. The near band-edge emission peak at 564 nm (LFC1) is assigned to be shallow-trapped exciton emission, it has a red-shift with the increase of the excited power due to the higher carrier concentration. Usually, the FX emission would be stable only if its exciton binding energy is over 26 meV. However, the exciton binding energy of ZnTe is just 12.6 meV lower than the thermal kinetic energy (KT) of 26 meV at room temperature. Hence,

the excitons in ZnTe can be easily separated by the scattering of phonon, carrier or defects. Thus it is not easy to observe FX emission at room temperature in ZnTe. The peak at 572 nm (LFC2) is regarded as the EMP which is related to the interactions with phonons and spins and it can be confirmed in the following.

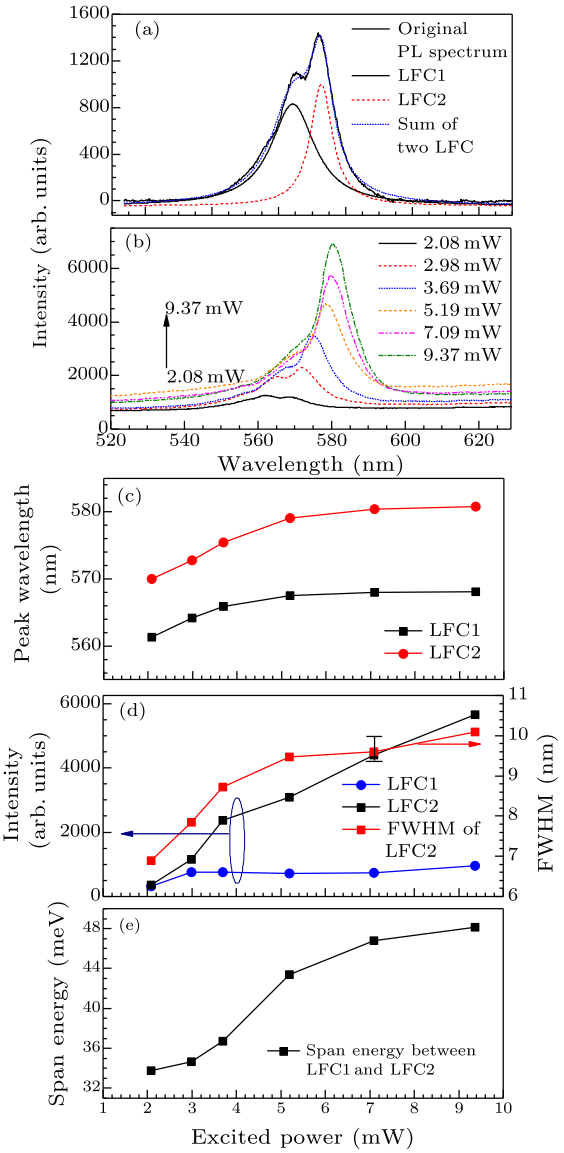


**Fig. 4.** (a) The fitted PL spectra of the emission with the Lorentz function at excitation power $P = 2.98$ mW. The black spectrum is the original PL spectrum. The LFC1 and LFC2 are fitting spectra of the Lorentz function curves. The blue curve is the sum of two LFCs. (b) The PL spectra at different excitation powers (2.08–9.37 mW) in room temperature. (c) Power-dependent spectra of the peak wavelength of LFC1 and LFC2. (d) Full widths at half maximum (FWHM) of EMP (LFC2) at different excitation powers (filled squares, red). The power-dependent intensity curves of LFC1 (filled circles, blue) and LFC2 (filled squares, black). (e) The span energy between LFC1 and LFC2 with the increase of the excitation power.

The PL spectra of Co-doped ZnTe nanowire for different excitation powers (2.08–9.37 mW) at room temperature are obtained in Fig. 4(b). With the increase of the excitation power, the emission intensity increases as more carriers are produced, accompanied with larger electron-electron scattering. Hence, the emission bands have a significant red-shift effect. The red shift of emission bands comes from two reasons. First, the high excitation power activates a large number of photoinduced carriers that are responsible for the bandgap, which collide and scatter with each other and even form an electron-hole plasma.[19–22] For the narrow-bandgap semiconductor, the exciton binding energy of ZnTe (12.6 meV) is less than the thermal kinetic energy KT (26 meV), thus excitons are easy to dissociate into electron holes, and as power increases, electron-hole plasma is formed. Secondly, for the high excited power, photon and exciton can move even with longer distances, thus the electron-phonon coupling range increases, which results in electronic scattering enhancement, hence leads to large red shift.

Actually, it may be confused regarding the EMP peak with LO phonon replica of shallow-trapped exciton emission. Firstly, the largest LO phonon energy is 26 meV in ZnTe materials,[23] which is not in agreement with the energy span between peaks of LFC1 and LFC2 in this nanowire. Thus the emission at the long wavelength side of the band-edge emission band is EMP instead of the LO phonon replica emission. Previous studies interpret the formation and emission of EMP in TM ion doped Ⅱ–Ⅵ semiconductors, indicating the emission at the long-wave side of FX. There is a double-peak structure in the range of 540–580 nm, and the emission of EMP appears due to the coupling between free excitons and ferromagnetic spins out of transition metal ions. In the early report of Liu *et al.*,[5] the emission of EMP is also observed in $Mn^{2+}$ doped ZnO nanowires because of the Mn-Mn direct spin ferromagnetic coupling. The EMP could be found in other reports, for example, the Co doping in CdS nanobelts,[9] the Fe(Ⅲ) and Mn doping in ZnSe,[6,7] Mn doped CdS microwires also observed double-peak in PL spectra.[24] With the increase of the excitation power, the luminescence intensity of EMP could be significantly enhanced compared with that of the shallow-trapped exciton emission peak, indicating that EMP is increasing in number due to the higher binding energy. Secondly, as shown in Fig. 4(c), at the beginning, the emission of EMP also has a red shift due to the dominant carrier scattering. However, when the intensity of EMP increases with power, the peak position becomes more stable, indicating the strong spin binding effect. EMP becomes even dominant at high concentration due to high stability, thus the peak has no red shift accompanied by an increasing intensity. In the system of ZnTe:Co nanowires, the contribution of carriers have been overcome at high excitation, and EMP dominates the luminescence.

With the increasing power, the FWHM of EMP increases nonlinearly as shown in Fig. 4(d) with red curve, which is related to the phonon scatterings. Meanwhile, the enhancement of photoinduced carri-

ers contributes to more electron-electron collision and electron-phonon coupling, leading to broadening the FWHM of EMP. In addition, the span energy between two peaks becomes broader with the increasing excitation power just as shown in Fig. 4(e). It lies in that the propagation distance of phonon is enhanced, which means increasing electron-phonon coupling at higher excitation. Therefore, we obtain that EMP is related to FX interactions with both phonons and spins, but not only FX with coupled spins.

In narrow bandgap materials, the carrier effect is often important due to phonon scattering. The photoinduced carriers will generate when the stoichiometric ratio of zinc and tellurium is close to 1:1 and Co ions concentration is lower. The free exciton binding energy of ZnTe is 12.6 meV, which is substantially smaller than KT (phonon scattering energy of 26 meV), thus free exciton related emission cannot be observed at room temperature. Only when the exciton binding energy is more than 26 meV, excitons can be stable at room temperature. The binding energy of EMP in ZnTe:Co is greater than 44.7 meV at room temperature. Thus it could be observed in this system. Moreover, the intensity of EMP is increased quickly at high excitation power due to their larger binding energy and coherent collective transition process. As a result, the existence of EMP not only increases the stabilization of the bound excitons, but also enhances the luminescence intensity. With the increasing power, photoinduced carriers make less contribution than the EMPs to band-edge emissions, which results in the dominant EMP emission and diminishes the influence of photoinduced carriers. Hence, in the case of the stoichiometric ratio of zinc and tellurium approaching 1:1, low Co (Ⅱ) doping can effectively generate EMP excitations.

In summary, Co(Ⅱ) doped ZnTe nanowires have been synthesized by the CVD method, which is confirmed by their SEM images and PL spectra. In this system, the EMP emission band dominates, accompanied by the near band-edge emission band, especially at high power excitation. Its occurrence of the emission band indicates that the Co-Co direct spin ferromagnetic coupling is present in this system, in contrast to that doped with Mn(Ⅱ) and Ni(Ⅱ). This high stability excitation EMP is valuable to the tuning of luminescence and lasing in DMS and will be found in applications in spin-polarized photonic devices in the future.

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