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Room temperature enhanced red emission from novel Eu\textsuperscript{3+} doped ZnO nanocrystals uniformly dispersed in nanofibers

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Abstract
Achieving red emission from ZnO-based materials has long been a goal for researchers in order to realize, for instance, full-color display panels and solid-state light-emitting devices. However, the current technique using Eu\textsuperscript{3+} doped ZnO for red emission generation has a significant drawback in that the energy transfer from ZnO to Eu\textsuperscript{3+} is inefficient, resulting in a low intensity red emission. In this paper, we report an efficient energy transfer scheme for enhanced red emission from Eu\textsuperscript{3+} doped ZnO nanocrystals by fabricating polymer nanofibers embedded with Eu\textsuperscript{3+} doped ZnO nanocrystals to facilitate the energy transfer. In the fabrication, ZnO nanocrystals are uniformly dispersed in polymer nanofibers prepared by the high electrical field electrospinning technique. Enhanced red emission without defect radiation from the ZnO matrix is observed. Three physical mechanisms for this observation are provided and explained, namely a small ZnO crystal size, uniformity distribution of ZnO nanocrystals in polymers (PVA in this case), and strong bonding between ZnO and polymer through the –OH group bonding. These explanations are supported by high resolution transmission emission microscopy measurements, resonant Raman scattering characterizations, photoluminescence spectra and photoluminescence excitation spectra measurements. In addition, two models exploring the ‘accumulation layer’ and ‘depletion layer’ are developed to explain the reasons for the more efficient energy transfer in our ZnO nanocrystal system compared to that in the previous reports. This study provides an important approach to achieve enhanced energy transfer from nanocrystals to ions which could be widely adopted in rare earth ion doped materials. These discoveries also provide more insights into other energy transfer problems in, for example, dye-sensitized solar cells and quantum dot solar cells.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO is a wide bandgap (3.36 eV) semiconductor material with a large exciton binding energy (60 meV). It has been considered as an excellent candidate for optoelectronic applications, including light-emitting diodes, laser diodes, photodetectors, and so on [1, 2]. Among those applications, a white light-emitting ZnO diode has attracted enormous attention recently due to its exciton and chemical stability. In such an application, realization of three basic color emissions (namely blue, green and red) is fundamental for implementing various optoelectronic devices. Unfortunately, although blue and green emissions as well as UV emission have been reported [3–9], intense red emissions from ZnO are still lacking.
Rare earth (RE) ion doping could provide sharp light emission due to the special electron orbital structure of REs. Among RE activators, \( \text{Eu}^{3+} \) is widely used in light-emitting devices [10–12]. However, there are few studies of the use of intense \( \text{Eu}^{3+} \) emission from ZnO films, ceramics and powders [13–15]. It is found that the \( \text{Eu}^{3+} \) emission is always very weak and usually overlapped with strong defect emissions from the ZnO matrix. One of the main reasons is that it is hard to substitute \( \text{Zn}^{2+} \) by \( \text{Eu}^{3+} \), due to the much larger ion radius of \( \text{Eu}^{3+} \) (\( 1.05 \) Å; \( \text{Zn}^{2+} \), 0.74 Å). In particular, because the crystal size of ZnO is small (\( \sim 10 \) nm), where the quantum confinement effect manifests itself the nanocrystals show a self-purification effect and the dopant atoms are generally impelled to the outer surface of the nanocrystals [16]. This makes the doping of \( \text{Eu}^{3+} \) inefficient and further reduces the red emission from \( \text{Eu}^{3+} \). Some other reasons have been proposed to explain the weak \( \text{Eu}^{3+} \) emission: a quenching effect of wide-band, self-activated, green or yellow emissions and the higher energy-level position of \( \text{Eu}^{2+} \) relative to the bottom conduction band (CB) [17].

Recently, preparation of a special structure and introduction of special surface defects in ZnO have been used to enhance \( \text{Eu}^{3+} \) emission [18, 19]. But the red emission is still not strong enough and is always accompanied by strong overlapped defect emission arising from ZnO. In addition, it is difficult to identify and tailor the type and density of defects that are useful for energy transfer from ZnO to \( \text{Eu}^{3+} \) among all the different possible types of defects [19]. Another way to obtain strong red emission without defect related emission is to introduce ZnO and \( \text{Eu}^{3+} \) into a silica matrix [20]. But the insulating properties of \( \text{SiO}_2 \) restrict its use electrically injected devices for optoelectronic applications. Other efforts have been made to develop synthetic approaches to improving the optical properties of doped nanocrystals by suppressing energy-loss processes at the surface of the nanocrystals [21–23]; however, efficient energy transfer from ZnO to \( \text{Eu}^{3+} \), resulting in an enhanced red emission at room temperature, is still a challenge.

In this work, highly efficient room temperature red emission is achieved from \( \text{Eu}^{3+} \)-doped ZnO nanocrystals with the help of polymer nanofiber assisted energy transfer. For the first time, efficient ZnO → \( \text{Eu}^{3+} \) energy transfer without orange defect emission at room temperature is observed. Three mechanisms for efficient energy transfer assisted by polymer nanofibers in the emission process are investigated, namely a small crystal size of ZnO, uniform distribution of ZnO nanocrystals in polymers (PVA in this case), and strong bonding between ZnO and \( \text{Eu}^{3+} \); by –OH group bonding. Resonant Raman scattering, high resolution transmission electron spectroscopy (HRTEM), photoluminescence (PL) and photoluminescence excitation (PLE) spectra are used to verify the analyses.

2. Experimental section

Highly dispersed \( \text{Eu}^{3+} \)-doped ZnO nanocrystals in polymer nanofibers were prepared beginning with a sol–gel aqueous solution. First, ZnO sol was prepared by dissolving 0.5 g zinc acetate dihydrate (Zn(CH\(_3\)COO\(_2\))\(_2\)H\(_2\)O) and 0.02 g europium nitrate hexahydrate (Eu(NO\(_3\))\(_3\)·6H\(_2\)O) into 1 ml deionized water under magnetic stirring. Then, another solution was prepared by dissolving 0.25 g poly(vinyl alcohol) (PVA; Sigma-Aldrich, \( M_w \approx 90000 \)) into 1 ml deionized water at \( 60 \) °C for 2 h under vigorous magnetic stirring to yield a clear and homogeneous solution. Subsequently, the first solution was dipped into the second one slowly an with additional 0.059 g acetic acid (CH\(_3\)COOH) added. Continuous stirring was performed for another 2 h to achieve a uniform solution. Finally, the precursor solutions were injected into an electrospinning apparatus which was assembled with a glass syringe, a stainless needle with an inner diameter of about 0.7 mm, a DC high-voltage source, and a grounded zinc flake. During the electrospinning process, the distance and the voltage between the needle and the zinc flake were 15 cm and 18 kV, respectively. Si substrates were placed on the zinc flake to collect the electrospun nanofibers. The highly dispersed samples were left at \( 120 \) °C in air for 12 h to allow water to evaporate. Then the samples were annealed at 300 or \( 600 \) °C in air for 2 h.

The morphologies of the samples were measured by field-emission scanning electron microscopy (FESEM; Hitachi S-4800) at an accelerating voltage of 5 kV and high resolution transmission electron microscopy (HRTEM; Philips CM300) operating at 300 keV. The structural properties of the samples were studied using a Siemens 101 D5005 x-ray diffractometer with Cu K\( \alpha \) (\( \lambda = 0.154 \) nm) radiation (40 kV, 40 mA). Micro-Raman spectra of the samples were recorded on a JY-HR800 micro-Raman spectrometer using a 325 nm wavelength laser. The PL properties of the ZnO nanofibers were measured by a Shimadzu rf-5301 fluorescent spectrophotometer and a spectrofluorophotometer (RF-540, Shimadzu Ltd) using the 325 nm line of a He–Cd laser as the excitation source. PLE spectra measurements were recorded by a Shimadzu rf-5301 fluorescent spectrophotometer. All the measurements were taken at room temperature.

3. Results and discussions

3.1. Field-emission scanning electron microscopy

In our work, PVA nanofibers with highly dispersed \( \text{Eu}^{3+} \)-doped ZnO nanocrystals were prepared by a high electrical field electrospinning technique. The samples were annealed at \( 300 \) °C and \( 600 \) °C in air for 2 h, respectively. Field-emission scanning electron microscopy (FESEM) images of highly dispersed samples and samples annealed at \( 300 \) °C and \( 600 \) °C in air are shown in figures 1(a)–(c), respectively. Ultralong nanofibers up to several centimeters can be prepared by this method. For the highly dispersed and \( 300 \) °C annealed samples, the surface of the nanofibers is smooth and the diameter is about 200 nm. For the sample was annealed at \( 600 \) °C, the diameter of the nanofibers obviously decreased to several tens of nanometers, which is due to the degeneration of the organic materials existing in the nanofibers. Moreover, it is obvious that the nanofiber consists of intensively doped...
Figure 1. FESEM images of (a) the highly dispersed sample, (b) the 300 °C annealed sample and (c) the 600 °C annealed sample. The insets are the high magnification pattern of the three samples. (d) EDS of the highly dispersed sample.

ZnO nanocrystals. Figure 1(d) shows the results of energy dispersive spectroscopy (EDS) of the highly dispersed sample. The presence of Eu³⁺ ions with a content of 2.51 at.% is confirmed.

3.2. X-ray diffraction

The crystal structure of samples was investigated by x-ray diffraction (XRD) as shown in figure 2. The annealed samples show a typical wurtzite structure. But for the highly dispersed samples the signals of ZnO are not clear, which might be due to its low content in the hybrid fibers (about 20% according to the DTG thermal analysis result) [24]. The average grain sizes of ZnO for the 300 and 600 °C annealed samples are estimated by the Scherrer formula

\[ D = \frac{0.89\lambda}{B \cos \theta} \]

where \( D \), \( \lambda \), \( \theta \) and \( B \) are the mean grain size, the x-ray wavelength of 0.154 056 nm, the Bragg diffraction angle and the full width at half maximum (FWHM) of (100), (002) and (101) peaks, respectively. The result shows that the average grain size increases from 7 nm (300 °C annealed sample) to 20 nm (600 °C annealed sample).

3.3. Resonant Raman scattering

Resonant Raman scattering spectra were first used to investigate the characteristics of ZnO nanocrystals and PVA in the nanofibers as shown in figure 3. For the PVA nanofibers, two Raman modes are observed at 1405 and 1605 cm⁻¹. The 1405 cm⁻¹ Raman peak arises from the superposition of OH and CH₂ bending motions and the 1605 cm⁻¹ Raman peak is attributed to the carbonyl stretching vibration [25, 26]. Both OH and CH₂ groups belong to the side chains of PVA, so the two Raman peaks represent the information from the side chains of PVA. These two peaks are obviously found in the highly dispersed sample as shown in figure 3, indicating that the PVA is maintained in the nanofibers. But for the samples annealed at 300 °C, only very little of the side chain of PVA is
C–C) degrade around 300°C, the scission of C–O and the main chain (the scission of water from an H bond between PVA molecules, then the side chain). Previous report [24]. The PVA first begins to degrade by losing phthalic anhydride (PA) from the polymer backbone.

The three samples are very different. First, the FWHM of the 1LO phonon overtones of ZnO. This means that ZnO nanocrystal phonon peak shifts in the nanostructured ZnO [31]: one 1LO phonon peak is observed. In our experiments, the narrowing of the FWHM of the 1LO Raman peak indicates the increase in ZnO crystal size with the increase in the annealed temperature. Moreover, due to the decrease in crystal size, the phonons with larger k vectors can participate in the Raman scattering. These larger k vectors greatly enhance the intraband Fröhlich interaction, therefore the corresponding scattering cross section results in an increase in the LO multiphonon. Thus the samples with a smaller crystal size (highly dispersed one and one annealed at 300°C) have a much larger 1LO Raman peak than the sample with a larger crystal size (sample annealed at 600°C) [28]. It needs to be mentioned that a contradiction seems to be present between the highly dispersed sample and the 300°C annealed sample, where the small crystal size sample (highly dispersed one) presents a lower 1LO Raman peak than the larger one (see figure 3). In addition to the effect of the crystal size on the induced Raman scattering enhancement, defects could also strongly enhance Raman scattering [29]. When the size of the particle decreases to several nanometers, the inner defects become fewer and the surface defects could play a more important role. In our experiments, for the highly dispersed sample ZnO nanocrystals are embedded in the PVA nanofibers. Strong bond forms between the –OH group on the side chain of PVA and the surface or/and subsurface defect states of ZnO. Then the surface states could be effectively suppressed. When the sample is annealed at 300°C, most of the –OH groups are destroyed as shown in the Raman results, and the defects on the surface or subsurface of ZnO nanocrystals disappear. Thus the Raman scattering of intensity is dramatically enhanced by the defect induced scattering effect. Moreover, the integrated Raman intensity of the first LO phonon from the highly dispersed and 300°C annealed sample is larger than that of the second LO phonon. This is in contrast to ZnO single crystal case [30]. This may also contribute to the spatial confinement and the defect scattering as discussed above. When the sample is annealed at 600°C, the ratio between the second- and the first-order LO Raman scatterings increases to 2.16, which agrees with that of ZnO bulk crystal.

Generally, there are three main mechanisms that can induce phonon peak shifts in the nanostructured ZnO [31]: one is spatial confinement within the nanostructures; the second is

| Table 1. Wavenumber, broadening, the ratio of n-LO phonons, and ratios of 1LO between different samples found in resonant Raman scattering spectra. |
|---|---|---|---|---|
| 1LO (cm⁻¹) (FWHM) | 2LO (cm⁻¹) (FWHM) | I₁LO/I₂LO | I₁LOsample/I₁LO(600°C) |
| Highly dispersed sample | 573 (36) | 1149 (64) | 0.78 | 4.74 |
| 300°C annealed sample | 575 (30) | 1152 (62) | 0.74 | 3.43 |
| 600°C annealed sample | 577 (25) | 1155 (61) | 2.16 | 1 |

![Figure 3](image-url) The resonant Raman scattering spectra of PVA (green line), highly dispersed (blue line), 300°C annealed (red line) and 600°C annealed samples (black line).
phonon localization by defects (oxygen deficiency, zinc excess, surface impurities, etc); the last is laser-induced heating in nanostructure ensembles. A red shift appears for the 1LO and 2LO Raman scattering peak (1LO from 577 to 573 cm\(^{-1}\); 2LO from 1155 to 1149 cm\(^{-1}\)). In our case, the origin might be the spatial confinement and the surface states. The laser-induced heating effect could be ruled by the following. First, we carefully adopt a low energy density of the laser in the measurements. Second, the configuration of the experimental setup for all the samples measurement is the same. Third, the Raman peak of the side chain of PV A (whose degraded temperature is about 250\(^\circ\)C) appears, meaning that the laser-induced heating effect could be neglected.

3.4. High resolution transmission electron spectroscopy

The distribution of the ZnO nanocrystal in the polymer was characterized by HRTEM measurements as shown in figure 4. For the highly dispersed sample, the ZnO nanocrystals of about 3 nm are highly dispersed in polymer as shown in figure 4(a), which is due to the large electrostatic force in the preparation process and the existence of ‘fixative’ PVA. The –OH bonding on the side chain of PVA stabilizes ZnO nanocrystals and prevents them forming clusters. When the sample was annealed at 300\(^\circ\)C, –OH bonds were destroyed, then ZnO nanocrystals formed clusters as shown in figure 4(b). When the sample was annealed at 600\(^\circ\)C, the PVA was totally removed and ZnO nanocrystals aggregated as shown in figure 4(c). Moreover, the size of ZnO nanocrystal increased from 3 to 25 nm with the increase in annealing temperature which is close to the XRD results. All these results agree with the Raman analysis. According to figure 4(d), a clear crystal lattice appears, showing the ZnO nanocrystals grow in the \((\bar{1}010)\) direction with a spacing of 0.282 nm (no. 80-0075).

3.5. Photoluminescence spectra

The optical properties of the samples were investigated by the PL spectra as shown in figure 5. For the highly dispersed sample, a peak around 435 nm is found, which may originate from the organic functional groups of PV A [24]. Moreover, it is found that strong Eu\(^{3+}\) ion red emissions are obtained and there is nearly no background emission from ZnO. It should be noted that this is the first time that such a strong red emission has been achieved with hardly any orange defect emission at room temperature. Former reports showed that Eu\(^{3+}\) ion emission in ZnO matrix is always very weak and the red emission always accompanied by strong orange defect emission from ZnO. The
two red emissions located at 592 and 617 nm come from $^{5}D_0 \rightarrow ^{7}F_1$ and $^{5}D_0 \rightarrow ^{7}F_2$ intra-atomic 4f–4f transmission of Eu$^{3+}$ ions, respectively. The optical property of the Eu$^{3+}$ ions is related to their location in the matrix material. It is well known that the transition $^{5}D_0 \rightarrow ^{7}F_1$ allows magnetic dipolar transition which is insensitive to the surrounding environment of the Eu$^{3+}$ ions. The Zn$^{2+}$ ions in the stoichiometric ZnO have the point symmetry of $C_{6v}$ [32]. Supposing that the Eu$^{3+}$ ions are strictly located at the sites of the Zn$^{2+}$ ions, as a consequence the Eu$^{3+}$ ions have the same symmetry $C_{6v}$ and the $^{5}D_0 \rightarrow ^{7}F_1$ transition band will be dominant and no other electric dipolar transitions ($^{5}D_0 \rightarrow ^{7}F_j = 0, 2, 4$) could be found [33]. As shown in figure 5, the appearance of the $^{5}D_0 \rightarrow ^{7}F_1$ emission from the Eu$^{3+}$ ions might indicate that some of the Eu$^{3+}$ ions are located at the Zn$^{2+}$ site in ZnO. For the electric dipolar transition $^{5}D_0 \rightarrow ^{7}F_2$, because the probability of the transition between the states with the same parity is zero, it is strictly parity forbidden. But this rule can be ignored when the site symmetry of Eu$^{3+}$ ions is noncentrosymmetric or low centrosymmetric such as at the nanocrystal surface or/and subsurface [33]. All these phenomena might be ascribed to the synthesis process of hybrid fibers. In the synthesis process of the highly dispersed sample, parts of the Eu$^{3+}$ dispersed in the solution might substitute the Zn$^{2+}$ sites in the as-grown nanocrystals. Moreover, due to the quantum confinement effect, the nanocrystals show a self-purification effect and then most of the Eu$^{3+}$ ions might be impelled to the surface of the nanocrystals. Thus the $^{5}D_0 \rightarrow ^{7}F_1$ (from the Eu$^{3+}$ ions on the substitutional site) and the $^{5}D_0 \rightarrow ^{7}F_2$ (from the Eu$^{3+}$ ions on the surface/subsurface site) emissions appear from the highly dispersed sample. When the sample was annealed at 300 °C, a sharp peak located at 394 nm and a broadband emission are found, which might be due to bound exciton emission [34]. Moreover, green and orange defect emissions appeared. In ZnO, two normal defects are the neutral oxygen vacancy (V$_{O}$) and the neutral zinc vacancy (V$_{Zn}$), and they change to V$_{O}^{\ast}$ and V$_{Zn}^{\ast}$ when losing one additional electron and to V$_{O}^{\ast\ast}$ and V$_{Zn}^{\ast\ast}$ when losing two electrons, respectively. Both V$_{O}^{\ast}$ and V$_{Zn}^{\ast}$ defects are acceptor defects when they are located in the depletion region where their energy levels are higher than the Fermi level [35–37]. Here the green emission is attributed to V$_{O}^{\ast}$ defects and the orange emission might be due to V$_{Zn}^{\ast}$ related surface states. When the sample is annealed at 600 °C, the broad emission spectrum changed, and the green emission centered at 520 nm became the dominant emission. Meanwhile, almost no Eu$^{3+}$ ion emission was found from the samples annealed at 300 or 600 °C.

According to the Raman results, the mechanism could be understood in the following way as shown in figure 6: in the highly dispersed sample (figure 6(a)), the ZnO nanocrystals with a very small nanocrystal size are uniformly dispersed in the PVA nanofiber due to the high electrical field during the preparation process as shown in figure 4 [24]. Strong bonds formed between the –OH group of PVA and the surface or subsurface states of ZnO. This bonding plays two roles: first, the surface defect, especially some acceptor defects could be strictly passivated [38–40]. Upon illumination at a photon energy above the band gap of ZnO, electrons in the valence band could be excited into the conduction band. Because there are nearly no acceptor defects, the electrons could diffuse to the surface of the nanocrystal and an accumulation layer may form [41–44]. As discussed above, most of the Eu$^{3+}$ ions reside on the surface of the ZnO nanocrystals. The accumulation layer could provide enough electrons transferring from ZnO to Eu$^{3+}$ ions on the surface. Thus a strong Eu$^{3+}$ emission without defect related orange emission could be achieved in the highly dispersed sample. Second, the bonding might stress the Eu$^{3+}$ ions attached to the ZnO nanocrystal, and this may also enhance the energy transfer between ZnO nanocrystals and Eu$^{3+}$ ions.

When the sample was annealed at a high temperature (600 °C) the crystal size of ZnO increased and the PVA was totally removed from the nanofibers. Large ZnO particles aggregated together as shown in figure 6(b). For the large ZnO nanoparticles, lots of defects may occur inside and/or outside the nanocrystals. Without the PVA capping, the surface of the particle exposed to the air could absorb more oxygen molecules. These oxygen molecules will capture electrons and a depletion layer would occur on the surface of particle [45]. In the fraction of this region where the Fermi level ($E_F$) passes below the V$_{O}^{\ast}$, all oxygen vacancies will be in the V$^{\ast\ast}_O$ state [35, 37]. This situation will also occur for zinc vacancies. So there will be large number of acceptor defects inside and/or outside the nanocrystals. When the sample was excited, the electrons in the valence band were excited into the conduction band and then captured by the V$_{O}^{\ast}$ defects (V$_{O}^{\ast}$ + e$^-$ → V$_{O}^{\ast\ast}$, then V$_{O}^{\ast\ast}$ + h$^+$ → V$_{O}^{\ast\ast}$ + green emission) and annihilated in the depletion layer. Thus there are nearly no electrons that could transfer to the Eu$^{3+}$ ions that reside on the surface of particles. Strong defect emission without any Eu$^{3+}$ ion emission from the 600 °C annealed sample proves this explanation. This model could also explain why it is always hard to obtain RE$^{3+}$ emission in a ZnO matrix and the emissions are usually accompanied by strong ZnO defect emission [33]. Additional evidence comes from the
Figure 6. The schematic structures of (a) highly dispersed sample and (b) 600 °C annealed sample: distribution of ZnO nanocrystals in the nanofiber, the surface states of ZnO nanocrystal and the energy band diagrams of ZnO nanocrystal.

300 °C annealed sample, where green and orange emissions originating from the inside and outside of the acceptor defects appear, due to the loss of –OH groups on the surface of the nanocrystals.

In summary, the achievement of strong red emission from Eu³⁺ doped ZnO in our experiment could be attributed to three points. The first is the small nanocrystal size. When the ZnO nanocrystal size decreases to several nanometers, the surface defects become dominant compared to the inner defects. Electrons could diffuse to the surface layer of the nanocrystals upon illumination. The second is the uniform distribution of ZnO nanocrystals in the polymers. This could prevent nanocrystals from aggregating together, thus avoiding the occurrence of surface defect states. The third is due to the presence of –OH bonding. This bonding could passivate the acceptor defects which lead to the defect overlap emission.

3.6. Photoluminescence excitation spectra and selected excited photoluminescence spectra

To investigate the process of energy transfer, the PLE of the 5D₀ → 7F₁ and 5D₀ → 7F₂ emission were also determined. Because there is almost no defect emission around 600 nm in the PL spectrum as shown in figure 5, the absorption in the PLE measurement could be regarded as direct energy transfer from ZnO to Eu³⁺ ions. As shown in figure 7, two absorption peaks appear at 394 nm and 464 nm, which is attributed to the bound exciton of ZnO and intra-atomic 4f–4f absorption of Eu³⁺ ions, respectively. It is noted that the energy of the bound exciton is exactly near the 5L₆ → 7F₀ energy of the Eu³⁺ ions, thus a resonant energy transfer might occur. In the PLE spectrum of 5D₀ → 7F₂, another absorption band appears at around 360 nm related to the near band gap absorption of ZnO. To confirm the PLE results, as shown in figure 8, different wavelengths are used to excite the highly dispersed sample. When the sample is excited at the 394 nm corresponding to the absorption peak in figure 7, characteristic Eu³⁺ ion emissions at 592 and 617 nm appear, which are consistent with the results.
of the excitation spectrum. No defect related emission from ZnO is found which might be due to the passivating effect of –OH groups. A similar phenomenon is also observed when the sample is excited at 464 nm. Moreover, as shown in figure 8, the 394 nm light is more effective than the 464 nm light for Eu$^{3+}$ ion excitation which agrees with the PLE analyses. To explain the energy transfer mechanism from the ZnO host to Eu$^{3+}$ ions, a schematic drawing is presented as shown in figure 9. For the sample annealed at 600°C, the electrons were excited to the conduction band and captured by acceptor defects ($V_{O}^{**}$ and $V_{Zn}^{**}$), resulting in green and orange emissions. No energy transfer occurred between ZnO and Eu$^{3+}$ ions. For the highly dispersed sample, photon absorption leads to the transition of electrons from the valence band to the conduction band of ZnO. Then the electrons transfer to the excited states of Eu$^{3+}$, resulting in red emission. On the other hand, the electrons interact with the LO phonon and finally in the form of free or bound excitons. These electrons transfer nonradiatively to the $^5D_0$ or $^5L_6$ level of Eu$^{3+}$ ions, leading to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emissions.

4. Conclusions

In summary, ultralong Eu$^{3+}$ ion doped ZnO nanocrystals uniformly dispersed in polymer hybrid nanofibers were prepared by a high electrical field electrospinning technique. Strong Eu$^{3+}$ ion red emission and almost no defect emission from ZnO were obtained for the first time. To investigate the origin of this behavior, the samples were annealed at 300 and 600°C, corresponding to no –OH group bonding and no PVA in the nanofibers, respectively. Resonant Raman scattering measurements were performed to investigate the crystal size and defects of the ZnO nanocrystals. It was found that the strong red emission is attributed to three mechanisms: the small crystal size, uniformly embedded ZnO nanocrystals in PVA and the –OH group bonding. This work not only provides an intense red emission from ZnO nanocrystal, but also proves the possibility of realizing other RE ion doped efficient emission in different materials which could be further utilized in various optoelectronic applications. In addition, one can also choose different polymers to realize various functionalities, for example, a conducting polymer can be used in the development of liquid crystal displays. It is also applicable to biological applications where biological identity can be used if we choose a polymer with special function group that is bonded to the examined bio-samples.

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