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COEB PHOTONICS
COEB - Centre for OptoElectronics and Biophotonics

Energy transfer efficiency from ZnO-nanocrystals to Eu^{3+} ions embedded in SiO_2 film for emission at 614 nm

Abstract

In this work the energy transfer mechanism from ZnO nanocrystals (ZnO-nc) to Eu^{3+} ions is studied by fabricating thin-film samples of ZnO-nc and Eu^{3+} ions embedded in a SiO_2 matrix. The samples were prepared using the low-cost sol-gel technique and were analysed using the time-resolved photoluminescence (TRPL) measurements, which was used to calculate the contribution of energy transfer from the various ZnO-nc emission centers to Eu^{3+} ions. The decay time obtained from the TRPL measurements was used to calculate the energy transfer efficiencies from the ZnO-nc emission centers, and these results were compared with the energy transfer efficiencies calculated from steady-state photoluminescence (PL) emission results. The results in this work show that high transfer efficiencies from the excitonic and Zn defect emission centers is mostly due to the energy transfer from ZnO-nc to Eu^{3+} ions which results in the radiative emission from the Eu^{3+} ions at 614 nm, while the energy transfer from the oxygen defect emissions is most probably due to the energy transfer from ZnO-nc to the new defects created due to the incorporation of the Eu^{3+} ions.

Key Results and Discussion

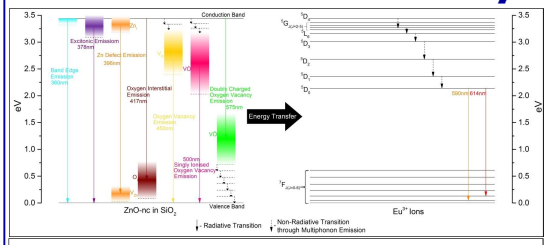

Figure 1: Energy band diagram showing the energy transfer from ZnO-nc to Eu^{3+} ions in SiO_2 together with the various transitions corresponding to the emissions from ZnO-nc and Eu^{3+} ions. The seven emission centers of ZnO-nc in SiO_2 are:

1. 360 nm: Band edge emission from ZnO-nc which possibly experiences quantum confinement effect (QC)
2. 378 nm: Excitonic emission (EE)
3. 396 nm: Zn interstitial to Zn vacancy defect (Zn_i to V_{Zn})
4. 417 nm: Oxygen interstitial defect(O_i)
5. 450 nm: Oxygen vacancy (V_o)
6. 500 nm: Singly ionised oxygen defect (V$\dot{O}$)
7. 575 nm: Doubly charged oxygen defect (V$\ddot{O}$)

The TRPL spectra of two types of thin-film samples; namely ZnO-nc in SiO_2 (ZnO-nc:SiO_2) and ZnO-nc with 12 mol% Eu^{3+} ions in SiO_2 (Eu^{3+}:ZnO-nc:SiO_2) were analysed to study the energy transfer efficiency from the seven different ZnO-nc emission centres to the Eu^{3+} ions. The nature of these seven ZnO-nc emission centers is schematically shown in the energy band diagram of Figure 1. The TRPL spectra were measured at each of the peak wavelengths of the seven ZnO-nc emission centers. However, the TRPL signals from the last three longest wavelengths, namely at 450, 500 and 575 nm, were weak compared to the other four emissions at 360, 378, 396 and 417 nm. Figure 2 shows the normalized TRPL spectra of the 378 nm ZnO-nc emission centers where we clearly see that the PL intensity of the sample with the Eu^{3+} ions decays faster than the sample without Eu^{3+}. The decay of the PL emission in the ZnO-nc:SiO_2 sample is due to the radiative and non-radiative de-excitation processes in the ZnO-nc. However, the decay of the PL emission in the Eu^{3+}:ZnO-nc:SiO_2 sample has additional components that contribute to the decay rate, namely (i) the energy transfer from ZnO-nc to Eu^{3+} ions which results in the radiative emission from Eu^{3+} ions at 614 nm, and (ii) the energy transfer from ZnO-nc to the additional new defects created due to the incorporation of the Eu^{3+} ions. To calculate the energy transfer efficiency from the ZnO-nc emission centers, the decay time (τ) of the TRPL emission was obtained by mathematically fitting the TRPL intensities using the stretched exponential decay fitting function, $I(t) = I_o e^{-\left(\frac{t}{\tau}\right)^{\beta}}$. Figure 2 shows the stretched exponential fitting curves, whose fitting parameters, namely the decay time (τ) and stretching exponential coefficient (β) values for all four measured TRPL of ZnO-nc emission center is shown in Table 1. β ranges from 0 to 1 and is a measure of interaction between identical ZnO-nc emission centers. τ was used to calculate the energy transfer efficiency from each of the ZnO-nc emission center using the formula $(E_T^{TRPL}) = 1 - \frac{\tau^{Eu^{3+}:ZnO-nc:SiO_2}}{\tau^{ZnO-nc:SiO_2}}$. This energy transfer efficiency was then compared with the transfer efficiency calculated from the steady-state PL emission using the formula $(E_T^{PL}) = 1 - \frac{I^{Eu^{3+}:ZnO-nc:SiO_2}}{I^{ZnO-nc:SiO_2}}$. Figure 3 shows these transfer efficiency values. Combining the results of spectral overlap integrals from our previous work with the transfer efficiencies results of this work, we deduce that the high transfer efficiencies E_T^{PL} and E_T^{TRPL} of EE and Zn_i to V_{Zn} emission centers are mostly due to the energy transfer from ZnO-nc to Eu^{3+} ions and not to the additional new defects created due to addition of Eu^{3+} ions. We also observe that the oxygen defect emissions of ZnO-nc such as O_i, V_o, and V$\dot{O}$, the values of the transfer efficiencies E_T^{PL} and E_T^{TRPL} are similar to those of EE and Zn_i to V_{Zn} emission centers, even though the spectral overlap integral values of oxygen defect emissions are low. This implies that the energy transfer from these oxygen defect emission centers is mostly due to the energy transfer from ZnO-nc to the additional new defects created due to the incorporation of the Eu^{3+} ions. The formation of Eu^{3+} ion-induced defect centers is a very important result that needs to be considered when fabricating light-emitting devices which use the energy transfer process from ZnO-nc to excite RE ions. This result, together with the knowledge and understanding of ZnO-nc emission centers can help in fabricating energy-efficient red light-emitting devices.

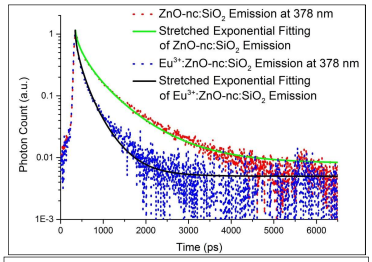

Figure 2: The time-resolved photoluminescence (TRPL) spectra of the ZnO-nc:SiO_2 and Eu^{3+}:ZnO-nc:SiO_2 samples measured at 378 nm along with their respective stretched exponential fitting curves.

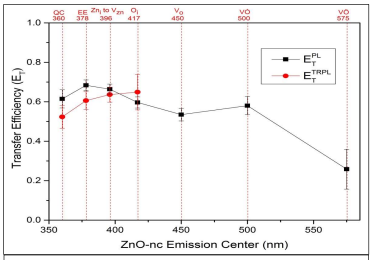

Figure 3: Transfer efficiency of ZnO nanocrystals emission centers due to the incorporation of the Eu^{3+} ions, calculated from the time-resolved photoluminescence (TRPL) spectra and steady-state photoluminescence (PL) emission data, along with their respective error bars.

Sample	Emission Wavelength	τ(ps)	β
ZnO-nc:SiO_2	360 nm	215 ± 8	0.65 ± 0.02
Eu^{3+}:ZnO-nc:SiO_2	(QC)	102 ± 7	0.69 ± 0.02
ZnO-nc:SiO_2	378 nm	213 ± 4	0.62 ± 0.01
Eu^{3+}:ZnO-nc:SiO_2	(EE)	84 ± 4	0.62 ± 0.01
ZnO-nc:SiO_2	396 nm	264 ± 6	0.61 ± 0.01
Eu^{3+}:ZnO-nc:SiO_2	(Zn_i to V_{Zn})	95 ± 5	0.61 ± 0.01
ZnO-nc:SiO_2	417 nm	356 ± 15	0.62 ± 0.02
Eu^{3+}:ZnO-nc:SiO_2	(O_i)	125 ± 10	0.62 ± 0.02

Table 1: The decay time (τ) and stretching exponential coefficient (β) values for the various ZnO-nc emission centers obtained from the time-resolved photoluminescence (TRPL) spectra of the samples with and without Eu^{3+} ions (Eu^{3+}:ZnO-nc:SiO_2 and ZnO-nc:SiO_2 samples, respectively)

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