Enhancement of band-edge emission induced by defect transition in the composite of ZnO nanorods and CdSe/ZnS quantum dots

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A new and general approach to enhance band-edge emission at the expense of defect emission in a semiconductor nanocomposite is proposed. The underlying mechanism is based on the resonance effect between defect transition and band-to-band excitation and transfer of excited electrons between conduction band edges. With our approach, it is possible to convert defect loss into bandgap emission. As an example, we demonstrate that the bandgap emission of ZnO nanorods can be enhanced by as much as 30 times when they are compounded with CdSe/ZnS nanoparticles. © 2008 Optical Society of America

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Defects can provide an additional channel for the relaxation of excited electrons and holes and reduce the quantum efficiency of useful bandgap emission. Therefore, defect loss is always considered a major obstacle for the fabrication of high-efficiency solid-state emitters. It exists inescapably in most materials and is very difficult to overcome. Here, we provide a new approach that can convert defect loss into bandgap emission in an appropriately designed semiconductor nanocomposite. The underlying mechanism involves the resonance effect between defect transition and bandgap excitation and transfer of excited electrons between conduction band (CB) edges. To illustrate our proposed mechanism, a composite consisting of ZnO nanorods and CdSe/ZnS quantum dots (QDs) is fabricated and investigated. The ZnO nanorod is an interesting and potential candidate for UV light emitters owing to the increasing demands for short-wavelength light emitting diodes [1–4]. Its characteristic features include a large bandgap energy of 3.27 eV and exciton binding energy of 60 meV. However, there are several kinds of defect existing in ZnO, such as zinc vacancy V_{Zn} , oxygen vacancy V_O , and many others [5–7]. Hence, how to improve the efficiency of the bandgap emission is a challenging task. Previously, several efforts have been devoted to the improvement of the bandgap emission, but with only limited success [4,8]. In this Letter, on the basis of our new concept, we provide an alternative approach and demonstrate that the bandgap emission of a ZnO nanorod can be enhanced by up to 30 times.

In this experiment, ZnO nanorods were prepared by a vapor–liquid–solid process. A mixture of high-purity ZnO and carbon powders (the molar ratio is 1:1) were used for growth. The mixed powders were placed on an alumina boat, and the boat was placed at the center of a quartz tube. At the same time, the gold-coated sapphire was placed on the same boat at the distance from the powders of about 3 cm. Last, we put the quartz tube into the heater. The tube was heated to 980°C at a rate of 40°C/min. The reaction was maintained for about 60 min. After the furnace

was cooled, white and grayish-white products formed on the surface of the sapphire substrate [9]. Figure 1 shows the scanning electron microscopy (JSM 6500 JEOL) top view of the ZnO nanorods. We can see that the nanorods are well aligned and have an average diameter of 50 nm and a length of about 1 μ m.

On the other hand, CdSe/ZnS QDs were synthesized by a solgel process. Briefly, the typical synthesis procedure is as follows [10–12]. CdO and stearic acid were heated to 150°C under an argon flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. Tri-*n*-octylphosphine oxide (TOPO) and hexadecylamine were added to the flask, and the mixture was heated to 320°C under the argon flow to form an optically clear solution. Diethylzinc ($ZnEt_2$) and hexamethyldisilathiane [(TMS) 2S] were used as the zinc and sulfur precursors to form a ZnS shell overcoated with CdSe. Finally, we dissolved the nanoparticles into the methylbenzene solution with a concentration of 1%. A spin coating system was used to coat CdSe/ZnS nanoparticles onto ZnO nanorods.

Photoluminescence (PL) spectra for ZnO nanorods were excited by a He–Cd (325 nm) laser. The emis-

Fig. 1. Scanning electron microscope image of ZnO nanorods (top view).

Fig. 2. PL spectra of ZnO nanorods coated with CdSe/ZnS QDs (dashed curve) pure ZnO nanorods (solid curve), and pure CdSe/ZnS quantum dots ($\times 1/5$, dotted curve).

sion was dispersed by a Spex 0.85 m double-grating monochromator and detected by a cooled photomultiplier tube.

Figure 2 shows the PL spectra of pure CdSe/ZnS QDs, pure ZnO nanorods, and the composite of ZnO nanorods and CdSe/ZnS QDs. We can see that the main peak of CdSe/ZnS QD emission is at 570 nm. A weak bandgap emission of ZnO nanorods is seen at 380 nm, and a defect emission appears at around 540 nm [4,8,9]. Note that in this case the energy of the defect emission is not in resonance with that of the bandgap transition of CdSe/ZnS QDs. According to previous reports [4,8,9], the defect emission arises from an oxygen vacancy localized at the surface. As is shown in Fig. 2, for the PL spectra of the composite of ZnO nanorods and CdSe/ZnS QDs the emission arising from CdSe/ZnS QDs is substantially reduced by a factor of 15 times, while the bandgap emission of ZnO nanorods is enhanced by a factor of about 5 times. To illustrate the possible mechanism responsible for our observation, a band structure diagram is plotted in Fig. 3, in which the valence band (VB) of ZnO is defined at -7.39 eV and CB is at -4.19 eV of absolute vacuum scale (AVS). On the other hand, the VB and CB of CdSe bulk are at -6 and -4.3 eV, respectively [13,14]. Due to the quantum confinement effect, the actual energy levels of CB and VB of CdSe QDs are at the dotted lines as shown in Fig. 3 [15–17]. Note that the CB of CdSe QDs is higher than that of ZnO nanorods. When electrons were excited from the VB to the CB state in CdSe QDs, they are able to transfer to the CB edge of ZnO nanorods. Because the shell thickness of CdSe/ZnS QDs is only about 0.8 nm, electrons can easily tunnel through the ZnS barrier and enter the ZnO nanorod. Therefore, the bandgap emission of ZnO nanorods is enhanced, and that of CdSe/ZnS QDs is quenched.

To further improve the enhancement factor of the bandgap emission of ZnO nanorods, we have designed another sample having the unique property that the defect transition in ZnO nanorods is in reso-

nance with the bandgap excitation in CdSe/ZnS QDs. Figure 4 shows the corresponding PL spectra for this especially designed nanocomposite. Quite interestingly, it shows that the bandgap emission of ZnO nanorods can be greatly enhanced by more than 30 times, while the emission intensity of CdSe/ZnS QDs is again greatly reduced. It indicates that most of the energy is transferred from CdSe/ZnS QDs to ZnO nanorods and converted into bandgap emission. Together with the result shown in Fig. 2, we can rule out the possibility that the enhanced bandgap emission is due to the passivation of ZnO surface defects after ZnO nanorods compounded with CdSe/ZnS nanoparticles. That the energy conversion is most efficient when the defect emission is in resonance with the bandgap excitation of QDs suggests that the underlying mechanism responsible for the large enhancement may be related to the well-known phenomenon called fluorescence resonance energy transfer (FRET) [18].

FRET is an important mechanism for investigating a variety of biological phenomena that produce changes in molecular proximity [19,20]. There exist several excellent review papers [21–23]. Recently, FRET has also been applied to inorganic composites as well as inorganic–organic hybrid semiconductor nanostructures [24,25]. FRET is a distance-dependent interaction between the electronic excited states of two systems, in which excitation is transferred from a donor to an acceptor without emission of a photon. Transfer can be refereed by inductive resonance. The electronic interaction stimulating resonance energy transfer involves a coupling of transition processes of the donor and acceptor systems via a Coulombic interaction, which is similar to coupled oscillators. Early work also established that the basic requirements for FRET to occur include three main factors. Donor and acceptor molecules

Fig. 3. (Color online) Band alignment of ZnO nanorods and CdSe QDs, showing that carriers can transfer from CdSe/ZnS QDs to ZnO nanorods and enhance the bandgap emission of ZnO nanorods. It also shows that if the defect transition of ZnO is in resonance with the band excitation of CdSe, the defect loss may be converted into bandgap emission.

Fig. 4. PL spectra of pure ZnO nanorods (solid curve), pure CdSe/ZnS quantum dots ($\times 1/5$, dotted curve), and the composite of ZnO nanorods and CdSe/ZnS QDs (dashed curve). Here, the defect transition of ZnO nanorods is in resonance with the bandgap excitation of CdSe/ZnS quantum dots.

must be in close proximity. The absorption spectrum of the acceptor must overlap the fluorescence emission spectrum of the donor. Donor and acceptor transition dipole orientation must contain a parallel component. These three factors can be easily supplied by our specially designed nanocomposite. Therefore, under the FRET process, the excited carriers in the CB of QDs are increased, and there are more carriers able to transfer to the CB of ZnO nanorods. It thus leads to a large enhancement of the bandgap emission of ZnO nanorods.

In conclusion, we have provided a new approach that is able to enhance bandgap emission at the expense of defect emission in a semiconductor nanocomposite. To illustrate our approach, we have fabricated a composite consisting of ZnO nanorods and CdSe/ZnS QDs and demonstrated that the bandgap emission of ZnO nanorods can be enhanced by as much as 30 times. Besides the present example, this approach can become a general strategy for the design of many other nanocomposites with an enhanced bandgap emission, utilizing the three key concepts: (i) the defect transition in one of the constituents is in resonance with the bandgap excitation of the other one, (ii) the band alignment between the two elements enables the transfer of the electrons stimulated by defect transition into the CB edge of nearby material, and (iii) the interface area between the two materials in the composite should be as large as possible in order to maximize the transfer effect.

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