Giant enhancement of band edge emission in ZnO and SnO nanocomposites

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ZnO/SnO nanocomposites have been designed to enhance the band edge emission and suppress the defect emission of ZnO nanorods simultaneously. It is found that the intensity ratio between the band edge and defect emission can be improved by up to 4 orders of magnitude. The underlying mechanism is interpreted in terms of surface modification as well as carrier transfer from SnO nanoparticles to ZnO nanorods. Our approach is very useful for creating highly efficient optoelectronic devices. © 2006 Optical Society of America
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Electron transfer between semiconductor microparticles has been recognized and adopted as a fundamental process for enhancing the photoinduced charge separation in photocatalysis.¹ The general consensus is that electrons are transferred from the semiconductor with the higher conduction band (CB) to that with the lower CB. In particular, ultrafast charge separation led by electron injection from an electronically excited semiconductor with a higher CB to a semiconductor with a lower CB is a key step for improving the performance of semiconductor/semiconductor heterostructures.² Intuitively, light-emitting devices with heterostructure-based composites are expected to achieve higher lighting efficiency. However, in the study of nanomaterials, this concept has not received wide recognition.

Recently, much attention has been paid to ZnO nanostructures, owing to their wide bandgap energy of 3.37 eV and high excitonic binding energy of 60 meV.^{3,4} One of the obstacles to be overcome for the application of ZnO nanostructures in optoelectronic devices is how much we can reduce the defect loss and enhance the bandgap emission simultaneously. In early studies, the defect that arises from the O vacancies on a ZnO nanostructure surface is passivated by a surface layer of organic ligands,⁵ which is mainly used to avoid surface trap states that act as electron-hole recombination centers. In this study, to obtain a higher efficiency of light emission from ZnO nanostructures, we provide an alternative approach. We design a nanocomposite material that consists of ZnO nanorods and SnO nanoparticles. The SnO nanoparticles not only passivate the defects on the ZnO nanorods surface but also allow carrier transfer from SnO nanoparticles to ZnO nanorods. Quite interestingly, it is found that the band edge emission can be greatly enhanced and the defect emission can be substantially suppressed. The intensity ratio between the band edge and defect emission can be improved by up to 4 orders of magnitude.

ZnO nanorods were grown by the vapor-liquid-solid process by using a vacuum tube furnace, as reported elsewhere.^{3,4} SnO nanoparticles were prepared by using a sputtering system of magnetron type (JFC-1600, JEOL) with bulk tin metal as the sputtering

target. The existence of tin monoxide was confirmed by the Raman scattering measurement and band edge emission. The coverage of SnO nanoparticles was controlled by varying the sputtering times.

The morphology and composition of ZnO nanorods were characterized by scanning electron microscopy (SEM) (JSM 6500, JEOL) and an energy-dispersive x-ray spectrometer (Oxford). Photoluminescence (PL) spectra were obtained with two different systems. One of them uses the excitation from a 325 nm He-Cd laser, and the radiative emission was dispersed by a Spex 0.85 m double-grating monochromator and detected by a cooled photomultiplier tube. The other one uses a SPEX Fluorolog-2 instrument equipped with a double-grating monochromator and a R928 photomultiplier tube. The excitation source was provided by a 450 W Xe lamp whose output was focused into a 0.22 m monochromator to provide wavelength selection. Raman scattering measurements were made in the backscattering geometry utilizing a JOBIN YVON-SPEX (Model T-64000) micro-Raman spectrometer with the 632.8 nm excitation line of a He-Ne laser. The signal was detected by a liquid-nitrogen cooled CCD.

Figure 1(a) is the top view of the SEM image of the ZnO nanorods, and Fig. 1(b) is the SEM image at a tilt angle of 20°. The ZnO nanorods form a well-organized hexagonal shape grown on sapphire (*a* plane) with a diameter of 90–160 nm and a length of about 2 μ m. Energy-dispersive x-ray spectroscopic analysis reveals the molecular ratio of the ZnO nanorods to be 60.29% Zn and 39.71% O. Figures 1(c) and 1(d) show the SEM images of the ZnO nanorods with and without SnO nanoparticles. We can see that there are SnO nanoparticles on the surface of the ZnO nanorods.

To confirm the existence of SnO nanoparticles, we performed the Raman scattering measurement shown in Fig. 2. The peak at 300 cm^{-1} can be attributed to the E_u mode in SnO nanocrystals,⁶ which indicates that SnO semiconductor nanoparticles do exist on the surface of ZnO nanorods.

Figure 3 shows the PL spectrum of SnO nanoparticles sputtered on quartz with sputtering conditions

Fig. 1. Scanning electron microscopy images of (a) top-viewed and (b) tilt angle of 20° ZnO nanorods; (c) ZnO nanorods covered by SnO nanoparticles sputtered by a current of 20 mA for 450 s; (d) ZnO nanorods without SnO nanoparticles.

Fig. 2. Raman scattering spectrum of SnO nanoparticles.

similar to those for ZnO nanorods. We can see two clear emission peaks. The weak peak at 290 nm can be attributed to the bandgap emission of SnO nanoparticles,⁷ and the other strong, broad band at about 393 nm is due to the relaxation of electrons trapped in defect levels. Because of the O deficiency of the sputtering condition, the deep acceptor of anti-site oxygen O_{Sn} may be mainly responsible for the defect emission.⁸

Figure 4 shows the PL spectrum of the ZnO nanorods under 325 nm excitation. Before the deposition of SnO nanoparticles, the ZnO nanorods have a rather weak UV exciton emission at 380 nm and a strong, broad defect emission at around 518 nm. The defect emission is usually believed to be related to O vacancies.³ Surprisingly, after the deposition of SnO nanoparticles, the ZnO/SnO nanocomposites exhibit a quite different luminescence property from that of the pure ZnO nanorods. The UV emission intensity of ZnO nanorods is enhanced by more than one thousand times, and the defect emission is quenched substantially. Quite interestingly, the intensity ratio between the bandgap and defect emission can be improved by up to 4 orders of magnitude.

A straightforward interpretation for the above result is surface modification due to the SnO nanoparticles deposited on the ZnO nanorods. For instance, as was shown in several previous reports,^{5,9} the captured O atoms or SnO nanoparticles can have a strong chemical bonding with surface defects, which can greatly change the defect structures and bring about a clear passivation of the deep levels. Therefore, the defects cannot trap electrons again. Meanwhile, more energetic electrons in the conduction band recombine with the holes in the valence band; thus the UV emission is enhanced. However, this straightforward mechanism is not enough to explain the variation of PL spectra with pumping wavelengths as shown in Fig. 5. A maximum enhancement ratio of about 1200 times for the band edge emission at a pumping wavelength of 288 nm is observed. This photon energy is in good agreement with the bandgap transition of the SnO nanoparticles as shown in Fig. 3. We therefore point out that, in addition to the surface modification of ZnO nanorods, there exists a carrier transfer from SnO nanoparticles to ZnO nanorods. As the resonant absorbance occurs in the SnO nanoparticles, the excited electrons are able to transfer from SnO nanoparticles into ZnO nanorods, and maximal enhanced UV emission of ZnO nanorods is expected. Additional evidence for the existence of carrier transfer can be inferred from the re-

Fig. 3. PL spectrum of SnO nanoparticles sputtered on quartz.

Fig. 4. PL spectra of ZnO nanorods with and without SnO nanoparticles. The coating of SnO nanoparticles was sputtered by a current of 20 mA for 330 s.

Fig. 5. Variation of the intensity of the enhanced UV emission versus pumping wavelength.

Fig. 6. Energy band alignment for the ZnO/SnO coupled system. The photoinduced carriers can transfer from SnO to ZnO, which results in enhanced UV emission and achieves a maximum when the excitation photon energy matches the bandgap of SnO.

duction of the defect emission in SnO nanoparticles. As is shown in Fig. 3, a SnO nanoparticle has a large defect emission at 393 nm. But this spectrum completely disappeared when ZnO nanorods were present, as shown in Fig. 4. This may imply that the rate of the carriers' being transferred to ZnO nanorods is much faster than their being trapped in defects in SnO nanoparticles, which thus leads to the quenching of the defect emission in SnO nanoparticles and enhanced emission in ZnO nanorods. It is worth noting that, according to Fig. 5, when the excitation photon energy is away from and below the bandgap of SnO nanoparticles, the enhancement factor is about 200 times, whereas if the excitation photon energy matches the bandgap, the enhancement reaches the maximum value, a factor of 1200 times. This result indicates that the major contribution to the enhancement arises from surface modification, and the contribution due to carrier transfer is about six times.

To illustrate the above-mentioned mechanism, a schematic diagram is plotted in Fig. 6. In drawing

the band alignment, we have used the data in which the conduction bands of ZnO nanorods and SnO nanoparticles are located at -4.19 and -3.59 eV versus the absolute vacuum scale (AVS), respectively.⁷ Interestingly, according to the previous reports, it is known that the broad defect emission band in ZnO nanorods arises from the defect level to the valence band instead of from the conduction band to the defect level.³ Therefore, when SnO nanoparticles are in contact with ZnO nanorods, not only can the electrons and holes in SnO nanoparticles transfer to ZnO nanorods, but also the electrons in the defect level of ZnO nanorods can flow into the defect level of SnO nanoparticles. The latter process provides an additional channel for the quenching of the defect emission in ZnO nanorods as well as in SnO nanoparticles.

In summary, a novel semiconductor nanocomposite has been developed that consists of SnO nanoparticles on ZnO nanorods surfaces. It is found that the band edge emission of ZnO nanorods can be greatly enhanced and the defect emission can be substantially suppressed simultaneously. Surprisingly, the intensity ratio between the band edge and the defect emission can be improved by up to 4 orders of magnitude. The underlying mechanism is attributed to the fact that the SnO nanoparticles not only modify the surface of ZnO nanorods as a passivation layer but also lead to a carrier transfer from SnO nanoparticles to ZnO nanorods. The driving force for the carrier transfer is the relative energy of band alignment between the two semiconductors' nanostructures. Undoubtedly, our approach should be very useful in designing many other nanomaterial composites for creating varieties of high-efficiency optoelectronic devices, such as fluorescence biolabels, light-emitting devices, and laser diodes.

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References

1. R. Vogel, P. Hoyer, and H. Weller, *J. Phys. Chem.* **98**, 3183 (1994).
2. T. Haohua and F. K. David, *Int. Chem. Eng.* **6**, 116 (2006).
3. N. E. Hsu, W. K. Hung, and Y. F. Chen, *J. Appl. Phys.* **96**, 4671 (2004).
4. H. Y. Lin, C. L. Cheng, Y. Y. Chou, L. L. Huang, and Y. F. Chen, *Opt. Express* **14**, 2372 (2006).
5. N. Ohashi, T. Ishigaki, N. Okada, T. Sekiguchi, I. Sakaguchi, and H. Haneda, *Appl. Phys. Lett.* **80**, 2869 (2002).
6. S. Koval, R. Burrial, M. G. Stachiotti, M. Castro, R. L. Mingoni, M. S. Moreno, A. Varela, and C. O. Rodriguez, *Phys. Rev. B* **60**, 14496 (1999).
7. X. Yong and A. A. S. Martin, *Am. Mineral* **85**, 543 (2000).
8. B. X. Lin, Z. X. Fu, and Y. B. Jia, *Appl. Phys. Lett.* **79**, 943 (2001).
9. T. Gao, Q. H. Li, and T. H. Wang, *Chem. Mater.* **17**, 887 (2005).