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Origin of the green photoluminescence from zinc sulfide nanobelts

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ZnS nanobelts with a pure wurtzite phase have been synthesized by a thermal evaporation method with the assistance of H₂S in an Ar atmosphere. Photoluminescence band centered at about 535 nm has been observed under excitation in the range of 250–480 nm with decay rate as short as 860 ps. The origin of this intense photoluminescence is related to elemental sulfur species on the surface of the ZnS nanobelts. This assignment is substantiated by structural analysis by high-resolution electron microscopy, x-ray photoelectron spectroscopy, and photoluminescence and excitation technique. ZnS nanobelts with intense surface photoluminescence could be used as effective green light emitters, humid sensors, and UV light detectors. © 2004 American Institute of Physics. [DOI: 10.1063/1.1807018]

ZnS, as an important wide band-gap semiconductor, has attracted much attention owing to its wide applications, including UV light emitting diodes, efficient phosphors in flat-panel displays, and photocatalysis.^{1–3} Low-dimensional ZnS nanostructures, such as nanocrystals, nanorods, nanowires, and nanobelts, are expected to exhibit excellent optical and optoelectronic performances, which differ greatly from the bulk ZnS material.^{4–6} ZnS nanocrystals of various morphologies generally display a self-activated photoluminescence (PL) band centered at about 420 nm (originated from sulfur vacancies) or a near band gap PL band near 340 nm.^{7,8} Some groups also reported an additional green PL band centered at about 535 nm besides the self-activated blue band, and this green band has been ascribed to originate from the co-doping with copper and aluminum.^{9,10} Lee proposed that the green band from their ZnS nanobelts came from some defect states, although they provided no more information about their nature.¹¹ Kumbhojkar *et al.* studied the PL properties of ZnS clusters and assigned one of the blue shifted PL bands (may correspond to the green band in ZnS nanocrystals) as due to dangling orbitals of sulfur residing on the surface of the clusters,¹² however, they provided no more evidence for their assignment. Dunstan *et al.*¹³ systematically studied the photochemistry of ZnS colloids, and assigned a green PL band at 560 nm to elemental S species on the surface of ZnS particles. In this letter, we investigate the structural characteristics and the PL properties of the ZnS nanobelts, and provide evidence that the origin of the green band for ZnS nanobelts is indeed related to surface elemental S species.

ZnS nanobelts were synthesized according to the literature and under an experimental setup similar to previous work.^{11,14–16} The synthesis was carried out in an atmosphere of H₂S(20%)/Ar(80%) at 1100 °C for a heating time duration of 2 h with the gas flow rate of 40 sccm.

Figure 1(a) reveals a scanning electron microscopy (SEM) image of the as-synthesized ZnS nanobelts in a high yield with a width ranging from tens of nanometers to several micrometers and length up to tens to hundreds of micrometers. Figure 1(b) shows a transmission electron micro-

copy (TEM) image of the ZnS nanobelts. It can be observed that the nanobelts are long and straight with uniform width and thickness along the entire length. Dark lines on the nanobelts are bending contours similar to what Lee *et al.*¹¹ reported in their work. The energy dispersive x-ray spectrum (inset) shows that S and Zn are in an atomic ratio of 52.60%–47.40%. The high-resolution electron microscopy (HREM) image in Fig. 1(c) shows a perfect wurtzite structure with the spacings of the lattice planes 0.63 nm, corresponding to the separation between two (001) lattice planes of hexagonal

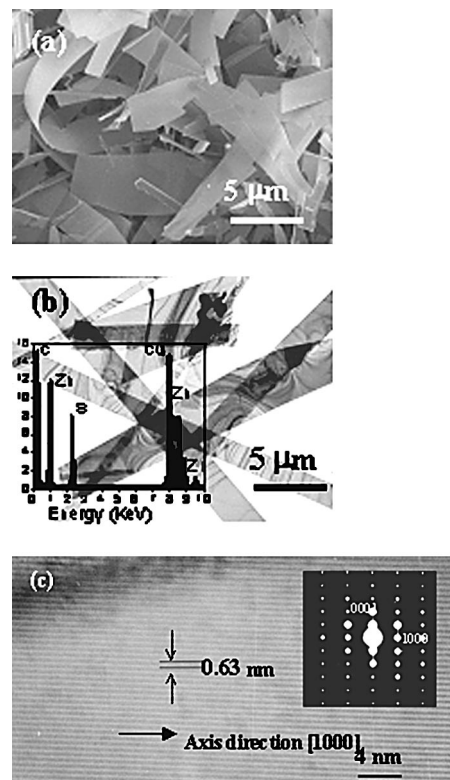


FIG. 1. (a) and (b) SEM and TEM images of the ZnS nanobelts, respectively. The inset in (b) displays that the nanobelts are pure ZnS, with atomic ratio of Zn to S as 47.40% to 52.60%. (c) HREM image of the ZnS nanobelts. The inset in (c) is a SAED pattern of the ZnS nanobelt taken along the (010) zone axis.

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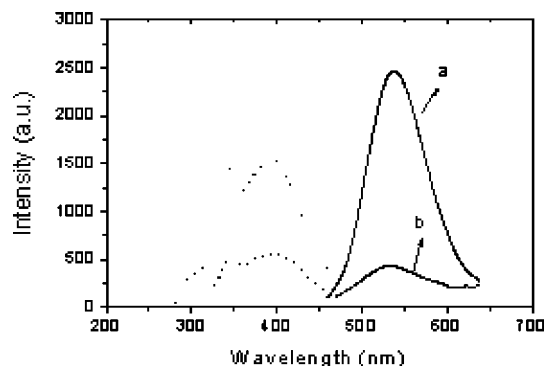


FIG. 2. PL and PLE spectra of the ZnS nanobelts. (a) PL recorded immediately, (b) PL recorded after a 30 min UV light illumination of the ZnS nanobelts (solid curve: PL spectrum, dotted curve: PLE spectrum).

ZnS. The selected-area electron diffraction (SAED) pattern (inset) taken along the [010] zone axis further proves the single crystallinity of the ZnS nanobelts.

Figure 2 (curve a, solid) shows the PL spectrum of the nanobelts with an excitation wavelength of 325 nm, where an intense green PL band centered at about 535 nm is clearly observed with no PL peak at around 420 nm being observed in the spectrum. With tuning the excitation wavelength from 250 to 480 nm the position of the green band has virtually not moved and the shape of the PL curve has remained essentially the same. The photoluminescence excitation (PLE) spectrum (curve a, dotted) exhibits two peaks at 340 and 400 nm, respectively. The peak at 340 nm corresponds to the band gap energy of ZnS, and the peak at 400 nm to defect energy levels. The PLE spectrum indicates that there is at least another defect state other than S vacancies in the band gap of ZnS nanobelts that can contribute to the green PL band.

Figure 3(a) shows the overall elemental composition analysis by x-ray photoelectron spectroscopy [(XPS), with sensing depth of 2 nm and detecting resolution of 0.01 at. %], where the atomic ratio of S to Zn is about 2:1. The enrichment of sulfur on the surface of the nanobelts is apparent. Figure 3(b) is the XPS spectrum of S (2*p*), where two peaks at 162.3 and 163.9 eV could be deconvoluted from the broad peak. The lower energy peak is due to S²⁻ and the higher energy peak is identified as elemental S species.¹³ The atomic ratio of minus divalent S to the elemental S species is about 1:4. The above data reveal explicitly that elemental S species are abundant on the surface of the ZnS nanobelts.

UV light annealing has also been reported to enhance or worsen the PL performance of ZnS:Mn²⁺ nanocrystals depending on the environment,¹⁷ owing to change of the surface structure of the nanocrystals. UV light (~3–4 eV) is high enough to initiate the photo-oxidation process on the surface of ZnS nanobelts and transform elemental S species to sulfur dioxides,^{12,18} henceforth, changing the surface structure of the nanobelts. If elemental S species on the surface of the ZnS nanobelts are indeed responsible for the green PL band, the intensity of this band should decrease after prolonged UV light treating. We measured the PL (Fig. 2, curve b, solid) and the PLE spectra (curve b dotted) after a 30 min illumination. Evidently, the intensities of the PL peak at 535 nm as well as the PLE peaks decrease greatly after the UV light illumination. On the basis of these results,

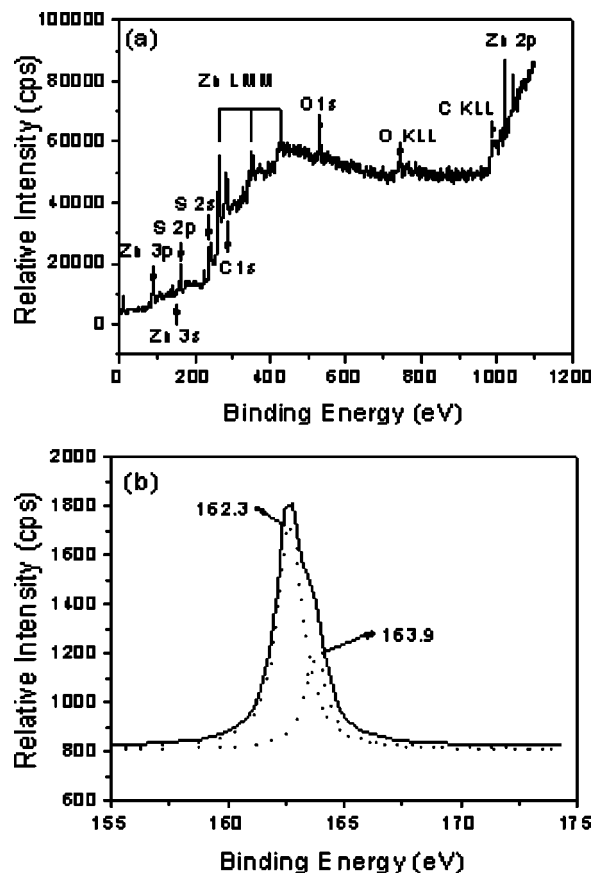


FIG. 3. (a) XPS survey spectrum of ZnS nanobelts, (b) S (2*p*) spectrum.

we can conclude that elemental S species on the surface of the ZnS nanobelts do contribute to the green PL band. However, it is noteworthy that the PL is very sensitive to the change of the surface structure (either the oxidation reaction or the structural transition of elemental S species), and minor change in the electronic configuration could lead to dramatic impact on the PL performance. Actually, we did not observe visible change in the XPS spectra after the UV light illumination (the oxidation of ZnS in dry air is slow; the detection sensitivity of PL is far better than that of XPS), which further supports the above conclusion.

Why did the self-activated blue band emission disappear for the ZnS nanobelts? Does Cu and Al co-doping rather than elemental S species on the surface of ZnS nanobelts contribute to the green PL band? To answer these questions, we further investigated the PL decay behavior. In Fig. 4, the lifetime (monitored at the PL wavelength of 535 nm) has a long time part of 7.46 ns and a short part of 860 ps. Monitoring at 420 and 610 nm gave similar results (differed slightly due to the energy difference at various wavelengths). These lifetimes are much shorter than that of the self-activated PL reported in the literature (on the scale of several tens to hundreds of nanoseconds¹⁹), therefore, the self-activated blue band emission could not compete with the elemental S related emission. We are able to preclude the contribution from either Ag and Al co-doping or Cu and Pb co-doping because the lifetime of the former system lies on the scale of microseconds,²⁰ and for the latter case hundreds of nanoseconds,²¹ whereas the lifetime of the ZnS nanobelts in the present study shows no microsecond part. Cu and Al co-doping may possibly have a decay lifetime comparable to the above two systems, and thus could also be discarded as

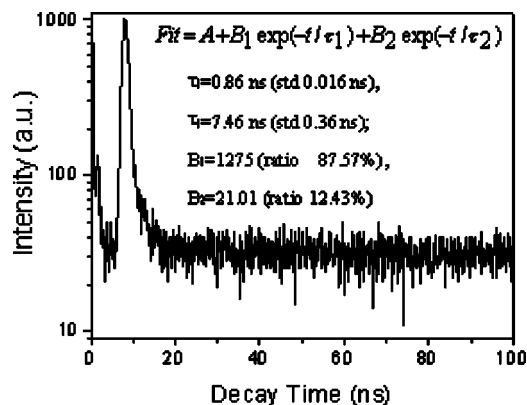


FIG. 4. The time decay of the light emission at 535 nm from ZnS nanobelts. The exponential decay can be separated into a longer part of 7.46 ns and a shorter part of 860 ps.

the origin of the green PL band at least for the present study. Furthermore, no metal dopants have been detected by XPS on the smallest scale of 0.01 at. % in the ZnS nanobelts. It is noteworthy that different ZnS nanostructures prepared by even the same researcher may possess a wide variety of surface structures; therefore, it is not surprising that the PL characteristics of these structures also varied. However, the exact configurations of the elemental S species on the surface of ZnS nanobelts have not been defined, and theoretical calculations are needed to elucidate the dynamics of electron-hole recombination processes involving this energy level.

In conclusion, it is shown that the origin of the green PL band at about 535 nm is related to elemental sulfur species on the surface of the ZnS nanobelts. The short lifetime of subnanosecond scale makes this PL band very efficient against the self-activated blue band, and also precludes the operation of Cu and Al co-doped emission. ZnS nanobelts with intense surface photoluminescence could be used as effective green light emitters, humid sensors, and UV light detectors.

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