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PAPER

Surface plasmon enhanced ultraviolet emission and observation of random lasing from self-assembly Zn/ZnO composite nanowires

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Self-assembly Zn/ZnO composite nanowires were successfully synthesized *via* a simple chemical vapor deposition method. The composition and crystal structure of the Zn/ZnO composite nanowires were characterized by transmission electron microscopy. The surface of the ZnO nanowires was decorated with Zn nanoparticles. Their photoluminescence properties were measured, indicating that the near-band edge emission intensity was significantly enhanced and visible emission was suppressed, which originates from the coupling between surface plasmons and the near-band edge emission of ZnO (or electromagnetic field). Random lasing from Zn/ZnO composite nanowires was observed due to the surface plasmon resonant effect. Our results show a convenient way to achieve laser action by the surface plasmon resonant effect.

With the wide band-gap of 3.37 eV, high exciton binding energy of 60 meV at room temperature and specific optical properties, ZnO is an excellent material for optoelectronic, sensing, piezoelectric application, solar cells, light emitting diodes and laser diodes.[1–8] However, ZnO usually shows low efficiency of the near-band edge (NBE) light emission, because a large number of electrons are trapped by surface states or impurities, which influences the application of optoelectronic devices. Hence, how to limit the emission related to these surface states or impurities is still a challenge. Recently, the resonant coupling between light or an electron-magnetic field and the surface plasmons (SPs) in metal nanoparticles (NPs) has turned out to be an efficient way to enhance the luminous efficiency of ZnO.[9–14] The most common way of enhancing the luminescence efficiency by surface plasmon resonance (SPR) is to cap a metal layer on the surface of ZnO. Several metals have been used as a capping layer to improve the NBE emission of ZnO nanostructure. The metals most frequently used are Pt,[10] Au,[11] Ag,[14] and so on. But the exorbitant price of these noble metals restricts their wide application. So the need to find some practical metals to use instead of these noble metals becomes an important issue. As an inexpensive metal, Zn could be more suitable for the enhancement of the NBE emission of ZnO than those noble metals. The reasons are as follows: (1) the absorption band for Zn is in the ultraviolet to visible spectral region;[15] (2) the oxygen affinity of the underlying metals such as Sn, Al, Pb, Te, Cu, Au, and Zn decrease in order.[16] Zn as a capping layer cannot lead to creation of new oxygen vacancies in ZnO; (3) the number of charge carriers transferred to ZnO depends on the difference in the value of the work function between a metal and ZnO. The work function of Zn (4.33 eV) is much smaller than that of ZnO (5.2–5.3 eV).[17] Therefore, more electrons in Zn NPs transfer to ZnO to form a strong local electric field at the Zn/ZnO interface, leading to a strong coupling between the SPs of Zn and the NBE emission light (or electromagnetic field) of ZnO. Although the Zn/ZnO core/shell structures have been studied,[18,19] the enhancement of the NBE emission of ZnO by SPR of Zn has not been reported up to now.

In this paper, we designed and synthesized Zn/ZnO composite nanowires by a one-step chemical vapor deposition (CVD) method, with Al and Au as catalysts. Here Zn NPs disperse on the surface of ZnO nanowires. Their photoluminescence (PL) properties were characterized. Significant enhancement of the NBE emission and random lasing from these nanowires were observed.

The self-assembly Zn/ZnO composite nanowires were synthesized via a simple CVD method. The mixture of Al and ZnO powders (molar ratio: 3:5) was loaded into one end of an alumina boat and the Au-coated Si substrate was placed at the other end, downstream of the mixture. The boat was placed inside an alumina tube that was inserted into a horizontal furnace, and the mixture was located at the center of the furnace. The furnace was heated to a preset temperature (1300 °C) under a flow of 200 sccm of nitrogen gas and a pressure of 500 Pa. The furnace temperature was kept for 20 min. Then, the furnace was naturally cooled to room temperature. The synthesized products were found covering the entire substrate. The morphology and composition of the products were characterized by scanning

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electron microscopy (SEM, S-4800) and high-resolution transmission electron microscopy (HRTEM, Philips Tecnai F20), equipped with energy dispersive X-ray (EDX) spectrometer. PL spectra were taken using micro-Raman system (J-Y HR 800, France), the 325 nm line of a He-Cd laser as the excitation source. The stimulated emission action was studied under optical excitation by a third harmonic generation of Nd:YAG 355 nm laser operating at a repetition rate of 1 Hz, with the full-width at half-maximum (FWHM) of 7 ns. The excitation laser focused onto the sample surface vertically. The spot size on the sample is about 100 μm. Light emission was analyzed with a 1200 lines mm^{-1} grating coupled to a spectrometer, coupled to a cooled CCD camera. The resolution limit of the detection system is 0.1 nm. All of the experiments were performed at room temperature.

X-ray diffraction data (not shown) demonstrate that the as-synthesized products have a hexagonal wurtzite structure. As shown in Fig. 1(a), a typical SEM image clearly reveals that random-growth oriented ZnO nanowires fully cover the substrate. The length normally exceeds 6 μm and the diameter is between 60 and 120 nm. The detailed morphology and microstructures of the as-synthesized nanostructures were further characterized by TEM. The inset of Fig. 1(a) shows a low-magnification TEM image of a single nanowire. With careful inspection, it can be seen that some NPs with diameters of about 5 nm are uniformity distributed on the surface of the ZnO nanowires. The microanalysis results on the nanowire side, the center of the nanowire and pure ZnO nanowire are shown in Table 1. The results confirm that the "the nanowire side" has a lower concentration of oxygen atoms. An EDX spectrum of the nanowire side is shown in Fig. 1(b), other EDX spectra are similar to Fig. 1(b) (not shown). So, these NPs on the nanowire mainly consist of Zn. Here these Zn NPs and ZnO nanowires self-assemble into Zn/ZnO composite nanowires. In this paper, this kind of nanowires with the NPs is called a Zn/ZnO nanocomposite. The high-resolution TEM results indicate that the nanowires grow along the $<10\bar{1}0>$ direction.

As in the previous reports,[9–14] the enhancement of the NBE emission and the suppression of the visible emission related to oxygen vacancies[20] for ZnO are related to the metal NPs. The main mechanism has been demonstrated to be SPR, some other factors have also been considered (*e.g.* surface modification, surface passivation and so on), but researchers proposed that these factors are not the primary cause.[10,11] The previous SPR enhancement mechanism summarizes charge transfer: the energy level of defect states with respect to the vacuum level in ZnO is higher than the Au Fermi level, leading to electrons transferring from the defect level in ZnO to the Au Fermi level. These electrons are excited by the SPR energy again and move to a higher level. Then, they can transfer back to the conduction band to participate in radiative recombination. Therefore, they concluded that the enhancement of the NBE emission and the suppression of the visible emission are due to the electrons in defect states transferring to Au NPs. In fact, there are many experimental results to confirm that the visible emission from ZnO is not fully suppressed.[9,14] Now, we propose a new mechanism to explain the enhancement of the NBE emission from ZnO on the basis of the previous SPR model.

Table 1 Atom percent of Zn and O for the nanowire side, the center of the Zn/ZnO nanocomposite, and pure ZnO nanowire, respectively

Element	Zn (At %)	O (At %)
The nanowire side	73	27
The center of nanowire	53	47
Pure ZnO nanowire	46	54

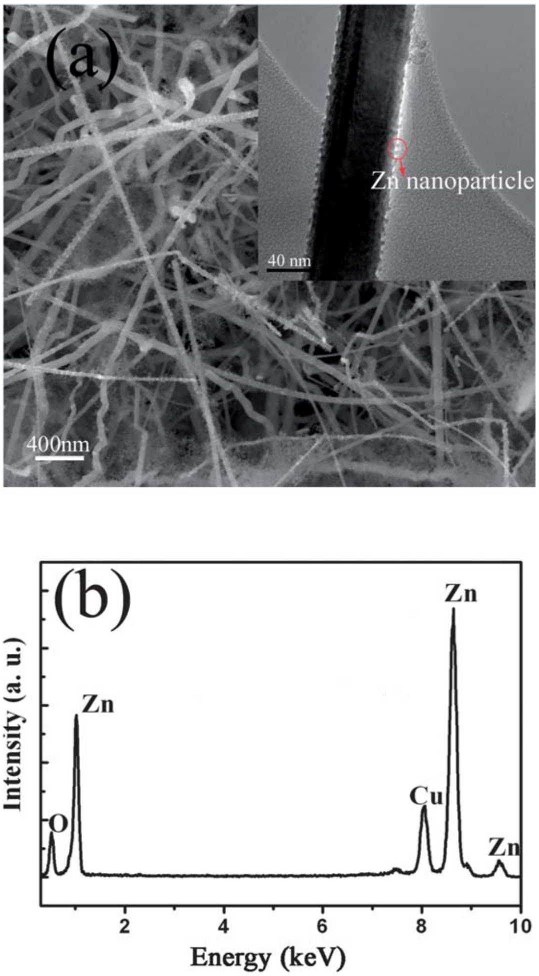

Fig. 1 (a) SEM image of the products. The inset shows the TEM image of a single nanowire. (b) EDX spectrum of the Zn/ZnO nanowire side.

In the present experiment, a Zn/ZnO nanocomposite is an integration of Zn NPs and ZnO nanowires. From ref. 15, Zn nanostructures show an absorption band centered at ∼380 nm with a broadening at longer wavelengths. This peak position is approximately equal to that of the NBE emission from ZnO. Why is the NBE emission from ZnO enhanced? In order to illustrate the enhancement mechanism more clearly, a schematic diagram is plotted in Fig. 2. Since the work function of Zn is smaller than that of ZnO (Fig. 2), the Fermi energy level of Zn is higher than that of ZnO. The integration of Zn NPs with a ZnO nanowire may lead to the transfer of electrons from these Zn NPs to the ZnO nanowire and accumulation of a number of electrons at the interface near the ZnO, while equal positive electrical charges remain at the interface near the Zn NPs. At thermodynamic equilibrium, a Fermi energy level aligns across the interface and local SPs are also formed at the interface, as shown in

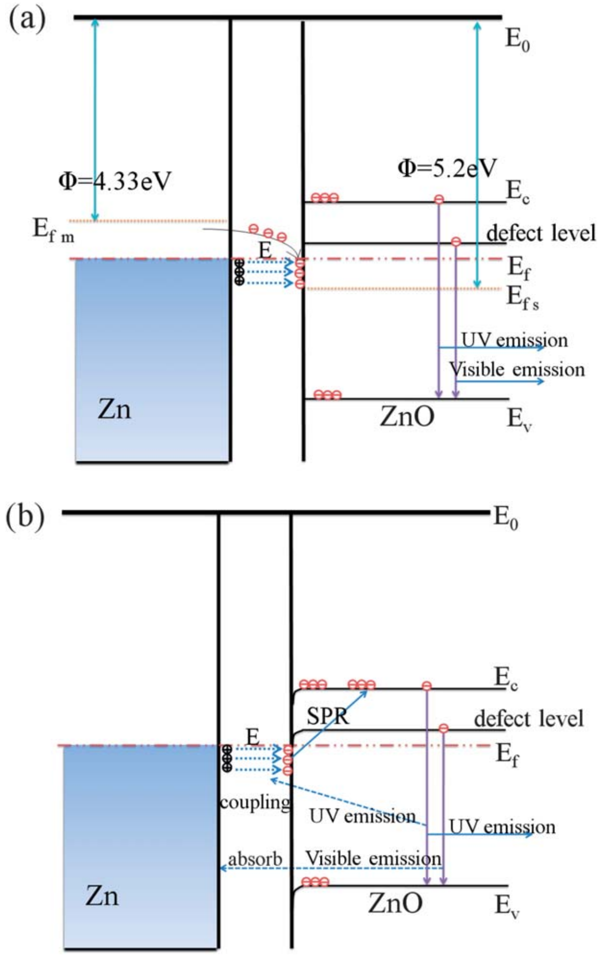

Fig. 2 The energy band structure of Zn and ZnO. (a) A Fermi energy level aligns across the interface and local SPs are also formed at the interface; (b) a local electric field leads to band bending, the electrons at the interface are excited by the SPR energy and move to the conduction band; the electrons at the defect level move to the valence band by a non-radiational process and the corresponding energy is absorbed by the Zn NPs. (Note, E_0: vacuum level; E_c: conduction band bottom; E_{fm}: Fermi level of Zn; E_f: uniform Fermi level; E_{fs}: Fermi level of ZnO; E_v valence band top; E: electric field).

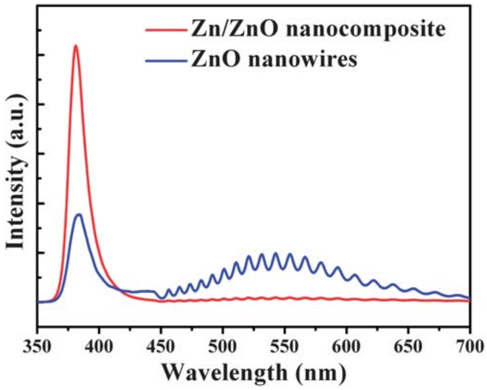

Fig. 3 PL spectra of the Zn/ZnO nanocomposite and ZnO nanowires, respectively.

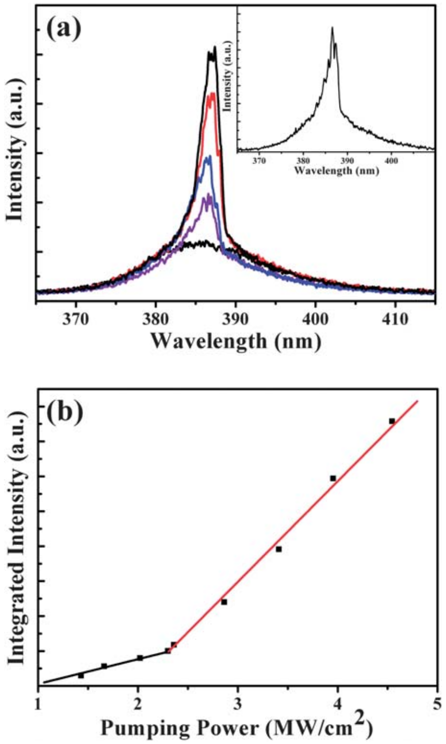

Fig. 4 (a) Excitation power dependence of the emission spectra of Zn/ZnO nanocomposite, the excitation intensity is (from bottom to top) 2.02, 2.86, 3.41, 3.95 and 4.5 MW/cm^2. The inset shows a typical stimulated emission spectrum under pumping power of 3 MW/cm^2; (b) integrated intensity as a function of the excitation power.

Fig. 2(a). Due to the existence of the local electric field, the band of ZnO bends downward, as shown in Fig. 2(b). Since the NBE emission energy of the ZnO nanowires matches the absorption peak energy of the Zn NPs, the local SPs occur resonant under the NBE emission light. These electrons at the interface are directly excited to the conduction band of the ZnO nanowires by the SPR energy, as shown in Fig. 2(b). Consequently, the increased electron density in the conduction band will lead to an increase in the hole–electron recombination rate. The NBE emission of the Zn/ZnO nanocomposite becomes enhanced. On the other hand, the electrons transferred from the Zn NPs to ZnO compensate the available surface states at the interface, which otherwise takes electrons from the interior. Due to the passivation of the surface states by the injected electrons, the concentration of electrons in the conduction band of ZnO will increase with respect to that without Zn NPs. Meanwhile, because the absorption spectrum of Zn shows a broadening at longer wavelength (380–600 nm) as mentioned above, the visible-range light emitted from the ZnO nanowires can be considerably absorbed by the Zn NPs. Hence, the visible emission is suppressed as shown in Fig. 3.

In order to provide further insight into the optical properties of Zn/ZnO, the PL spectra of the Zn/ZnO nanocomposite were measured under pulse excitation at room temperature. Fig. 4(a) shows a few typical PL spectra of the nanocomposite measured at various pumping powers. At low pumping power, only a spontaneous emission peak with a full width at half maximum (FWHM) of 16 nm is observed from the recombination of free excitons. With increasing the pumping power, a narrow emission appears due to the exciton–exciton collision process.[21] The narrowing of the PL peak and the concurrent increase of peak intensity with the increase of excitation power (Fig. 4(b)) indicate lasing action occurring. The lasing threshold is 2.3 MW cm^{-2}, which is close to the value of ZnO random-growth oriented nanowires.[22] The inset of Fig. 4(a) exhibits an emission spectrum at a pumping power of 3 MW cm^{-2}.

As is well known, the random laser emission in a disorder media of randomly oriented nanowires is a result of the coherent photon scattering that did not contain any conventional Fabry–Perot cavities.[23–25] In our experiment, random lasing observed in high-density the randomly grown Zn/ZnO nanocomposite is due to the high-gain characteristic of the Zn/ZnO nanocomposite and efficient light scattering in the Zn/ZnO nanocomposite, indicating that the laser action can be achieved more easily by the SPR effect in a metal–semiconductor nanocomposite.[26] The mechanism of the random lasing has been reported elsewhere.[22]

In summary, the Zn/ZnO nanocomposite was synthesized by a simple CVD method, in one step. The NBE emission was enhanced by SPR, while the visible emission was suppressed. We successfully observed the laser action in the Zn/ZnO nanocomposite.

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