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# Photoluminescence enhancement of ZnO microrods coated with Ag nanoparticles

## Haifei Lu, Xiaoliang Xu[1], Liu Lu, Maogang Gong and Yansong Liu

Structure Research Laboratory, University of Science and Technology of China, Chinese
Academy of Sciences, Hefei, Anhui 230026, People's Republic of China
and
Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026,
People's Republic of China

E-mail: xlxu@ustc.edu.cn

## Abstract
By sputtering a layer of 40 nm Ag film on ZnO microrods prepared by the aqueous solution
method, we observed photoluminescence enhancement from ZnO microrods coated with Ag
nanoparticles, comparing with pure ZnO microrods. The ratio of the enhancement, in particular,
reaches 6.6 at 396 nm. The enhancement mechanism is attributed to the special distribution of
the silver nanoparticle film, which is helpful for efficiently coupling the energy of electron–hole
pairs in ZnO microrods to the local surface plasmons (LSP) of silver particles and scattering the
energy of LSP into free space as a form of radiated light.

Recently, ZnO has attracted great attention for semiconductor optoelectronic device and ultraviolet (UV) laser device use, due to its wide and direct bandgap of 3.36 eV at room temperature and higher exaction binding energy (60 meV) [1–3], comparing to ZnSe (22 meV), ZnS (40 meV), and GaN (25 meV). But there are also some shortcomings of ZnO, such as the weak fluorescence and comparatively high excitation energy. In recent years, some research groups have concentrated on enhancement of the bandgap emission of ZnO by using the surface plasmons (SP) or localized surface plasmons (LSP) of various noble metals. Lai *et al* [4] and Ni *et al* [5] achieved 16-fold and 5.5-fold UV emission enhancement, separately, by coating the ZnO films with certain thicknesses of Al and Ag. You *et al* [6] sputtered ZnO film on Si(001) substrate which had already been coated with 100 nm Ag film previously, and the UV emission of the composite is found to be greatly enhanced. Cheng *et al* [7] also have shown 3-fold enhancement of bandgap emission of ZnO by coating the film with a layer of Ag island film.

However, the ZnO samples mentioned above are all prepared by RF magnetron sputtering, which imposes high demands on the equipment and the technological parameters

if we want ZnO to be used as the ultraviolet (UV) laser material. In comparison, ZnO microrods can be produced by a comparatively simple method, with a natural cavity [8]. Also the defect caused by the mismatch between the substrate and ZnO can be avoided [9]. Consequently, ZnO microrods have become among the most promising materials for ultraviolet (UV) laser use due to their natural structure and strong ultraviolet emission. But reports on the photoluminescence enhancement of ZnO microrods mediated by the surface plasmon still have not been published. In this paper, we will introduce an Ag nanoparticle/ZnO microrod coupling mode for obtaining the enhancement effect by emitting LSP.

The ZnO microrods were prepared in the following two steps [10]. (1) A 10 nm ZnO seed layer was first deposited on quartz substrates by the RF magnetron sputtering method. A commercially supplied ZnO ceramic plate with a purity of 99.99% was used as a target. The background pressure of the vacuum chamber was $1 \times 10^{-4}$ Pa. A mixed gas of oxygen and argon with a volume ratio of 1:1 was used as the sputtering gas with a total pressure of 3 Pa. The sputtering power and growth temperature were 100 W and 380 °C respectively. Then the two substrates coated with 10 nm ZnO film were annealed in the air at the temperature of 750 °C in order to form seeds for the microrods. (2) The two samples were placed vertically

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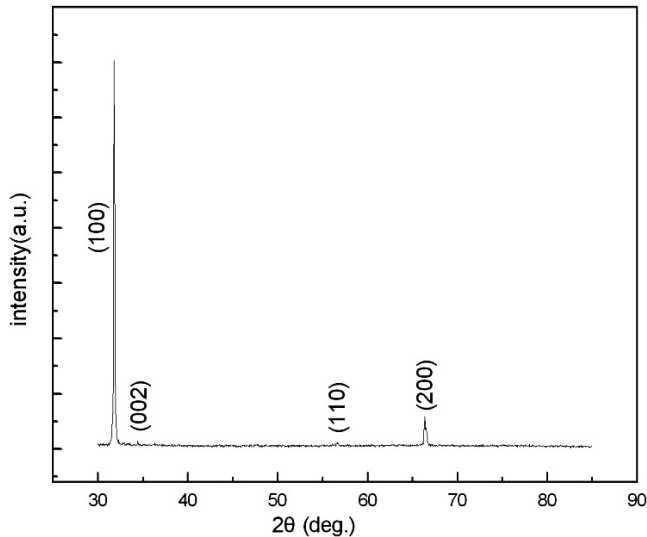[1] Author to whom any correspondence should be addressed.

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**Figure 1.** XRD pattern of the ZnO microrods grown on quartz.

was Ar at 3 Pa. The sputtering power and speed were 25 W and 40 nm min$^{-1}$ respectively.

X-ray diffraction (XRD) analysis was carried out with Cu K$\alpha$ (0.154 nm) as the incident radiation. The morphologies of the two samples growing with ZnO microrods and Ag/ZnO microrods were characterized by field emission scanning electron microscopy (FESEM). Photoluminescence (PL) spectra of the two samples were obtained with the excitation from a 325 nm He–Cd laser.

Figure 1 shows the XRD of the ZnO microrods grown on the quartz. According to the curve, the intensities of the (100) and (200) peaks are strong as compared to those of the (002) peak, which contrasts with the result of article [10]. However, the SEM image of the microrods in figure 2(a) can explain this contradiction well; in it, the microrods lie nearly on the substrate. In comparison, the microrods in the report [10] are perpendicular to the substrate. The orientation of (002) is perpendicular to (100) and (200). Therefore, the intensity of the (100) peak is stronger than that of the (002) peak. Also the XRD reveals that the microrods in our experiment are growing along the $c$-axis and have good quality structure.

Figure 2 shows SEM images of ZnO coated with or without Ag film separately. Figures 2(a) and (c) show the microrods without Ag deposited on the surface. The microrods, dispersed, lay on the substrate, 4–6 $\mu$m in length and 400–600 nm in diameter, and formed a perfect hexagonal structure. Figures 2(b) and (d) show the microrods with 40 nm Ag deposited on the surface. It is clear that the microrods in figures 2(a) and (b) show almost no difference—either in size or density. There is apparently a layer of Ag on the microrods in figure 2(d), and the roughness of the surface of the metal is quite high. Indeed, the film is composed of particles with the size 40–50 nm diameter.

into the solution, which was mixed with two aqueous solutions of the same volume: 0.01 mol l$^{-1}$ Zn(CH$_3$COO)$_2 \cdot$2H$_2$O and 0.01 mol l$^{-1}$ C$_6$F$_{12}$N$_4$, at the temperature of 90 °C for 3 h. Then the two substrates growing with ZnO microrods were picked out from the solution, washed in deionized water and dried.

Finally, the two ZnO microrods samples were annealed in air at the temperature of 400 °C for 1 h in order to eliminate the defects in ZnO. One of the samples had 40 nm Ag deposited on it by the RF magnetron sputtering method at room temperature. The background pressure was $5.0 \times 10^{-4}$ Pa. The working gas
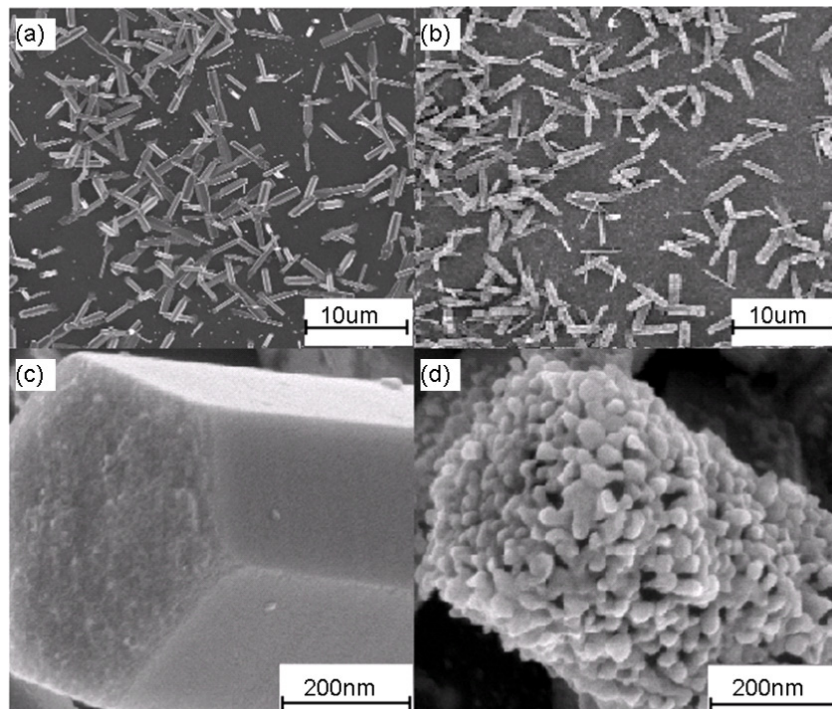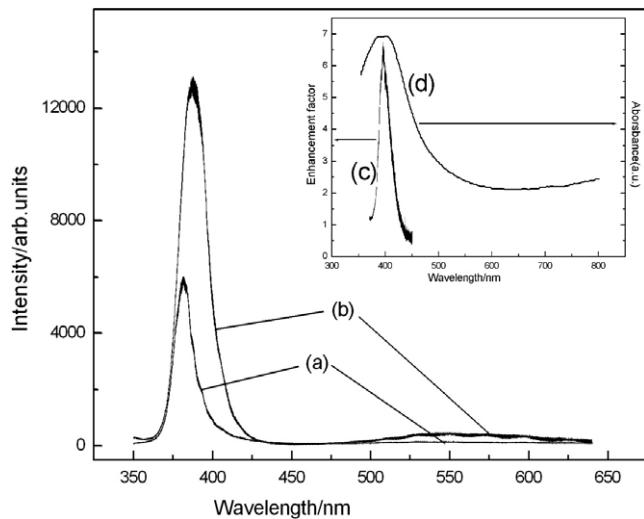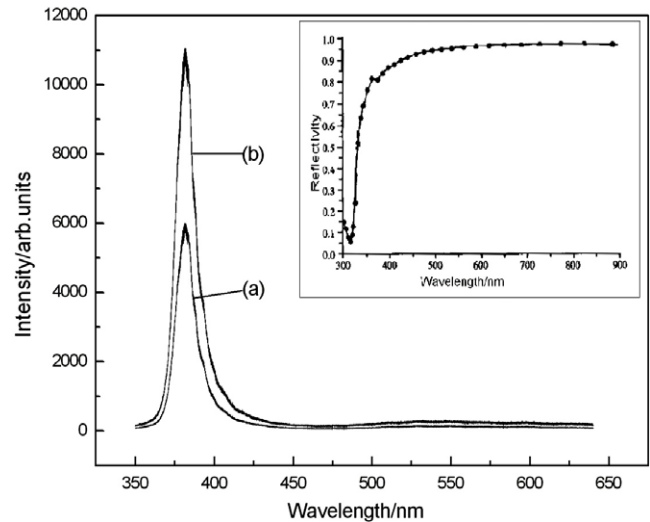


**Figure 2.** SEM images of ((a), (c)) ZnO microrods and ((b), (d)) ZnO microrods coated with separated Ag particles.

**Figure 3.** Photoluminescence spectra of (a) ZnO microrods and (b) ZnO microrods coated with 40 nm Ag. Insets: (c) the spectrum of enhanced ratios in the near ultraviolet region and (d) the absorption spectrum of Ag particles embedded in the $SiO_2$ film.



**Figure 4.** Photoluminescence spectra of (a) ZnO microrods and (b) Ag/ZnO microrods based on the hypothesis of the reflection of silver. The inset shows the spectrum of the reflectivity of a smooth silver surface.

The PL spectra of the two samples are shown in figure 3. The spectrum of the ZnO microrods is shown as curve (a). The peak positions at 381.6 nm with 87 meV full width at half-maximum (FWHM); this was attributed to FX-1LO [11, 12]. The emission for the visible light mostly caused by the defect in ZnO is very weak, indicating good quality of the ZnO microrods. Accordingly, the ZnO microrods are a good option for UV laser material use. Curve (b) in figure 3 is the spectrum of ZnO coated with 40 nm Ag film, showing a greatly enhanced photoemission of ZnO microrods. And the peak shifts from 381.6 to 387.6 nm. Such red-shifts of UV peaks of ZnO have also been reported by other research groups [4, 5]. Curve (c) shows the calculated (b)/(a) enhancement ratios in the near ultraviolet region.

The possibility of enhancement may be due to the reflection of the luminescence from ZnO by the Ag film between the ZnO rods. Spectrum (b) in figure 4 is the theoretical spectrum, calculated according to the photoluminescence spectrum of the ZnO microrods without Ag film and the reflectivity spectrum from a smooth silver surface [13] shown in the inset of figure 4. Comparing with spectrum (a), the peak position in spectrum (b) is seen to be the same: 381.6 nm. In perfect conditions, the best ratio of enhancement is 1.8 at 396 nm. The data obviously do not agree with our experimental result that the enhancement ratio reaches 6.6 at 396 nm and the peak shifts from 381.6 to 387.6 nm. Therefore, the possible enhancement from the reflection of the Ag film can be ignored. On the other hand, according to the previous work [14], the light enhancement could be attributed to the passivation of the surface states of ZnO as a result of coating with a layer of $AlO_x$ to suppress the emission of defects and consequently enhance the UV emission. However, the defect emission is very weak, as shown by curve (a) of figure 3. Therefore the passivation effect can be excluded from the enhancing mechanism in our case.

We obtained the optical absorption spectrum of Ag particles embedded in $SiO_2$ film of similar size to the particles coated on the ZnO microrods in our experiment. The peak of the absorption spectrum shown in figure 3(d), indicating the energy of LSP of Ag particles, stays at around 396 nm which coincides with the peak of the spectrum of enhanced ratios of various wavelengths shown as curve (c) of figure 3. Consequently, we can undoubtedly attribute the enhancement of the Ag–ZnO composite to the scattering of the LSP from the silver particles.

There are two mechanisms in the recombination of the excited electron–hole pairs of ZnO, as shown in figure 5(a): radiative and non-radiative recombination. The energy of electron–hole pairs will be transmitted as a form of radiated light in radiative recombination, while in the non-radiative recombination, the energy will be released as heat or some other form which cannot be detected by the spectrophotometer. When the pumping power density is lower than a certain threshold, the energy of non-radiative recombination is much greater than the radiative energy. This is also one of the reasons for the low efficiency of ZnO as a laser material. In contrast, when the ZnO is coated with a layer of Ag, there will be a drastic coupling of energy between the ZnO and surface plasmons (SP) because of the similarity of the bandgap of ZnO and the surface plasmon energy of the silver. The energy of the electron–hole pairs will be coupled into the SP of the silver film. Also the rate of the coupling is much higher than the rate of electron–hole pair recombination, as had been proved in previous work [15]. The SP of the silver film provide a kind of electromagnetic field which decays exponentially with distance from the surface and the energy cannot be scattered into free space. This is also the reason for the quenching effect in most cases of composites of semiconductors and noble metals.

However, this cannot happen in our experiment because of the special structure of the two materials, whose the interface
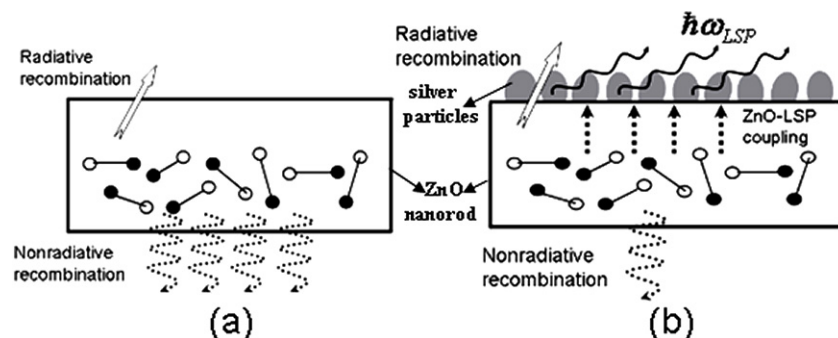
**Figure 5.** Schematic diagram of the electron–hole pair recombination of ZnO (a) without and (b) with Ag particles on the surface.

is shown schematically in figure 5(b). The structure can efficiently couple more energy of the electron–hole pairs to the free space than the emission of ZnO without Ag, and leads to photoluminescence enhancement for the composite. Firstly, as shown in figure 5(b), the excited light can reach the surface of ZnO microrods easily through the interspaces among the silver particles without much absorbance or scattering. Secondly, the energy of electron–hole pairs can be greatly coupled to the LSP of Ag particles in the vicinity of the energy between ZnO microrod UV emission and LSP of silver particles. Finally, the LSP energy can be coupled into the free space as radiated light because of the decrease in wavelength vector of the LSP caused by the scattering of the silver nanoparticles [16, 17].

In summary, we prepared ZnO microrods with good crystal quality on quartz by an aqueous solution method and deposited on the sample a layer of Ag particles with the size of 40–50 nm. The photoluminescence of the Ag/ZnO microrods is apparently stronger than that of the ZnO microrods without Ag film because of the intensive coupling between ZnO microrods and LSP of silver particles, which informs us of a good orientation for the composite of metal and semiconductor as a laser material.

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