

Enhanced ultraviolet emission of ZnO microrods array based on Au surface plasmon*

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In this work, the Au/ZnO hybrid microstructure was fabricated by assembling Au nanoparticles (NPs) onto the surface of ZnO microrods, and an obviously improved ultraviolet (UV) emission of ZnO is observed in the hybrid microstructure. About 27-fold enhancement ratio of the UV emission to the green band emission of ZnO is achieved. The underlying enhanced mechanism of the UV emission intensities can be ascribed to the charge transfer and the efficient coupling between ZnO excitons and Au surface plasmon (SP).

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At room temperature, the photoluminescence (PL) spectra of Zinc oxide (ZnO) usually consist of a narrow ultraviolet (UV) band and a broad green band. The UV peak is originally from the near band-edge (NBE) emission, and the green band is related to the defect states of oxygen vacancies^[1]. While a large portion of the excited charge carriers in ZnO is trapped in the defect energy states, resulting in a significant defect-related emission, which reduces the ultraviolet (UV) efficiency^[2]. Hence, how to improve the NBE emission as well as suppress the defect emission of ZnO is one of the research hotspots in the corresponding field.

Surface plasmon (SP)^[3] can lead to the field enhancement in the near-field zone of metal nanoparticles (NPs), and has many potential applications in surface-enhanced Raman scattering (SERS)^[4], biosensing^[5] and surface-enhanced fluorescence^[6]. Recently, SP enhanced emission has attracted great attention in the researches of LED and the luminescent semiconductors. For instance, Okamoto et al^[7] reported the improved quantum efficiency of InGaN quantum wells by cladding with Ag layer. Kirsty Leong et al^[8] obtained a 15-fold increase in brightness from biotin-quantum dots sandwiched between colloidal Au NPs and lithographically created metal nanoarrays. Also, SP assisted UV emission enhancement of ZnO was reported, and various metals and different composite structures have been introduced to realize this destination. For example, Xiao et al^[9] and Liu et al^[10] reported the UV emission enhancement of ZnO film decorated by Ag NPs and Pt NPs, respectively, and the enhancement factors reach to about 4 fold and 12 fold. While, in most of the reports, the

emission enhancement is generally attributed to the energy coupling between metal SP and ZnO excitons. However, the SP resonance position of metal NPs is generally located in the visible region, which is far from the wavelength of UV emission and the excitation of ZnO. It means that the coupling condition is mismatched and the evidence for the enhancement mechanism is insufficient. On the other hand, the metal particles used in most reports were fabricated by a complex process which are time-consuming and costly, so it is necessary to find a simple and economical method to fabricate the composite structure.

In this paper, the Au/ZnO hybrid microstructure was fabricated by a simple method of assembling Au NPs onto the surface of ZnO microrods, and the UV emission of ZnO is obviously enhanced in the hybrid microstructure. The underlying enhanced mechanism is also analyzed.

The ZnO microrods were synthesized on the Si substrate by a vapor phase transport (VPT) method^[11], and Au NPs used here were synthesized through reducing an aqueous solution of HAuCl₄ with NaBH₄^[12]. Then, the as-synthesized ZnO microrods was dipped into the solution containing Au NPs for 10 min. By the electrostatic forces, the Au NPs were decorated on the surface of the ZnO microrods, and the Au NPs/ZnO microrods composite was formed. After that, the sample was washed with deionized water to remove the residual chemicals. The morphology and structure of the samples were characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM). For optical measurements, the samples were excited by a

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325 nm femtosecond pulse laser, and the spectra were collected by an optical multichannel analyzer. All measurements were performed at room temperature.

Fig.1(a) shows the SEM image of ZnO microrods grown on the Si substrate. The diameters of the microrods are several to ten micrometers, and the lengths are about 1 mm. The microrods also present hexagonal cross-section and flat side surfaces as shown in Fig.2(b), which gives an magnified SEM image of a single ZnO microrod after being decorated with Au NPs. The SEM image of the Au NPs decorated on the surface of ZnO microrods is shown in Fig.1(c), from which it can be seen that the Au NPs with a uniform size of about 30 nm are better dispersion.

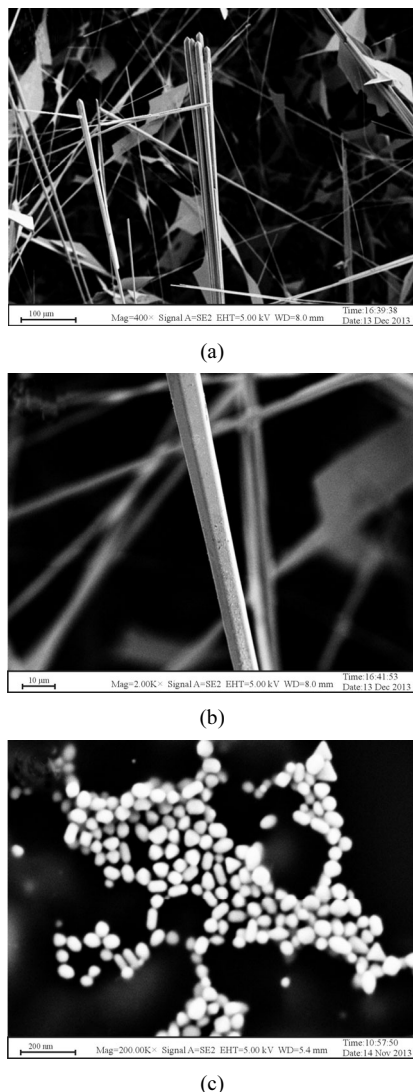


Fig.1 (a) SEM image of as-grown ZnO microrods array and the magnified SEM images of (b) Au NPs/ZnO microrods hybrid microstructure and (c) the Au NPs on it

TEM image of as-synthesized Au NPs is shown in Fig.2(a). It can be seen from Fig.2(a) that the diameters of the Au NPs are about 30 nm, and the Au NPs shows

better distribution with few aggregation. The inset of Fig.2(a) shows the high resolution TEM (HRTEM) image of a single Au NP with clear lattice fringes with d-spacing of about 0.24 nm, which is corresponding to the (001) lattice plane of the Au face-centered cubic structure.

In order to understand the influence of Au NPs on the optical property of the ZnO microrods, the UV-visible absorption spectra of as-synthesized Au NPs were measured in solution. As shown in Fig.2(b), the absorption peak is around 530 nm, which is far from the excitation wavelength of 325 nm and can be attributed to the SP resonance of Au NPs^[13,14]. It should be noted that the SP resonance position of Au NPs is very close to the photon energy of the green band emission of ZnO, which is also about 530 nm. This coincidence can lead to the suppression of the green band emission of ZnO due to the SP absorption and the enhancement of the UV band resulting from the electron transfer between Au NPs and ZnO microrods^[15].

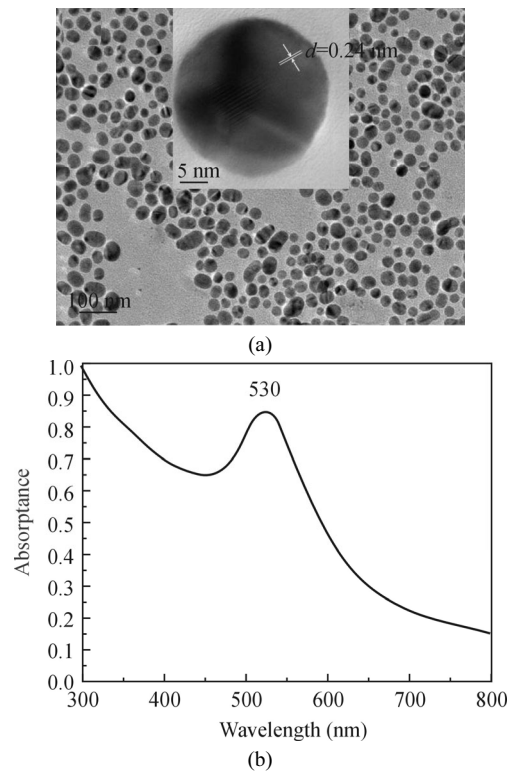


Fig.2 (a) TEM image of as-synthesized Au NPs (The inset shows the HRTEM image of a single Au NP.); (b) The absorption spectrum of the Au NPs

Fig.3(a) illustrates the room temperature PL spectra of the bare ZnO microrods at different excitation powers. It can be seen that the PL spectra all consist of a narrow UV band centered at around 390 nm and a broad green band centered at around 530 nm. For the bare ZnO, the intensities of the UV emission and the green band emission both increase with the increase of excitation

power. But the intensity ratio of the UV emission to the green band emission (I_{UV}/I_G) is quite different at different excitation powers. I_{UV}/I_G is about 1/3 at excitation power of 3 mW, while it is about 2 at excitation power of 30 mW. Thus, the intensity ratio of I_{UV}/I_G at excitation power of 30 mW is enhanced to about 6 times larger than that at excitation power of 3 mW.

After the ZnO microrods are decorated with Au NPs, the PL spectra of the Au NPs/ZnO hybrid microstructure change dramatically, as shown in Fig.3(b). It can be seen that the intensities of the UV emission and the green band emission both increase with the increase of excitation power, which is similar with that of the bare ZnO. But the enhancement for the UV emission is much faster than that for the green band emission. For the Au NPs/ZnO hybrid microstructure, the intensity ratio of I_{UV}/I_G is about 1/4 at excitation power of 3 mW, then it increases with the increase of excitation power, and reaches about 6.7 at the excitation power of 30 mW. The intensity ratio of I_{UV}/I_G for Au NPs/ZnO hybrid microstructure is enhanced to about 27 folds larger than that for the bare ZnO, as shown in Fig.3(c).

Combined with the UV-visible absorption spectrum of the Au NPs, the underlying mechanism of the dramatic enhancement ratio of the UV emission to the green band emission can be explained as follows. When the Au NPs/ZnO hybrid microstructure is excited with 325 nm laser light, ZnO will absorb the light and emit in UV and green band region. Due to the green band emission

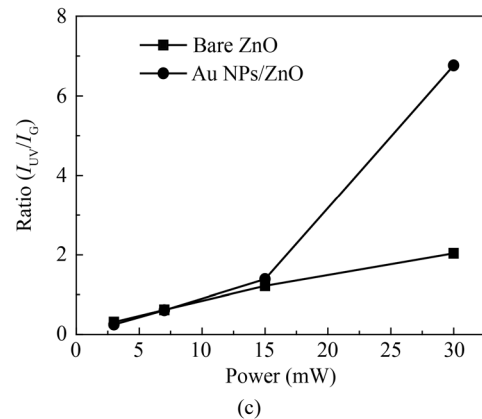
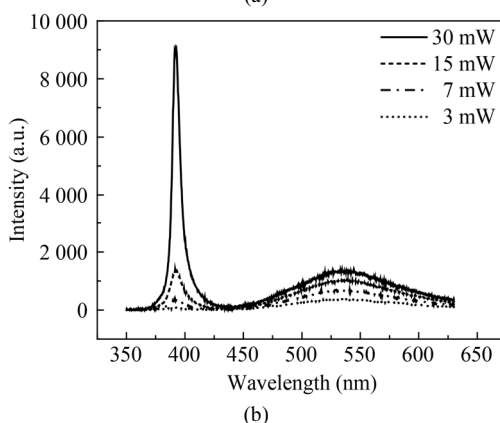
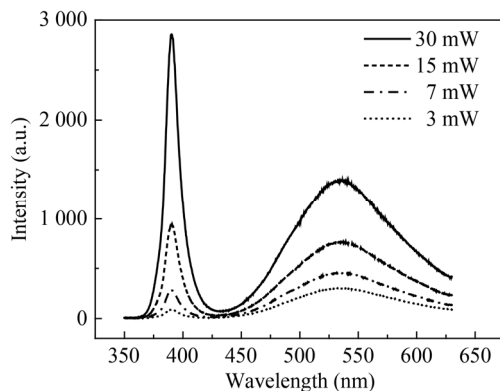


Fig.3 PL spectra of (a) the ZnO microrods array and (b) the Au NPs/ZnO microrods hybrid microstructure at different excitation powers; (c) The intensity ratio of the UV emission to the green band emission for ZnO microrods array and Au NPs/ZnO microrods hybrid microstructure at different excitation powers

energy of ZnO is very close to the SP absorbance energy of Au NPs, the emission energy can be absorbed by Au NPs, then the Au NPs get excited, and energetic electrons in higher energy states are produced in Au NPs. These active electrons can move to the conduction band of ZnO, which facilitates the radiative recombination process between electrons in the conduction band and holes in the valence band of ZnO, thereby resulting in an increase of the UV band emission intensity.

In summary, the Au/ZnO hybrid microstructure was fabricated by assembling Au NPs onto the surface of ZnO microrods, and the UV emission of ZnO is improved obviously in the hybrid microstructure. At excitation power of 30 mW, the intensity ratio of the UV emission to the green band emission is enhanced to about 27 folds larger than that for the bare ZnO. The underlying mechanism of the remarkably enhanced UV emission intensities can be ascribed to the charge transfer and the efficient coupling between ZnO excitons and Au SP.



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