Materials Letters 99 (2013) 97–100

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Optimization of UV emission intensity of ZnO nanoparticles by changing the excitation wavelength

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ARTICLE INFO

Article history:
Received 15 December 2012
Accepted 19 February 2013
Available online 27 February 2013

Keywords:
Zinc oxide
Semiconductors
Luminescence

ABSTRACT

Zinc oxide (ZnO) nanoparticles were prepared by using the sol–gel method with polyvinyl alcohol as surfactant. These ZnO nanoparticles exhibited excitation wavelength dependent photoluminescence (PL). PL spectra of ZnO were composed of different emission peaks at 384, 398, 418, 434, 467 and 492 nm depending on excitation wavelengths used. The maximum UV emission intensity was obtained when the excitation wavelength was chosen from the photoluminescence excitation (PLE) spectrum. The excitation wavelength selected from PLE is 353 nm; at this, there is more than 23 times enhancement in the UV emission intensity compared to 340 nm. At 370 nm excitation wavelength, UV emission at 398 nm was quenched completely.

1. Introduction

ZnO is a promising wide and direct band gap (3.37 eV) semiconductor which has potential applications in spintronics, ultraviolet (UV) and visible optoelectronics and also in bio-imaging [1–3]. Its large exciton binding energy of 60 meV ensures the stable exciton emission even at room temperature. But its use in UV devices is hindered by its low UV intensity due to undesired defect states. These defects give rise to a broad band at around 530 nm termed as green emission. Inspite of decades of research on ZnO, the origin of green emission is still controversial. Recent studies of Sharma et al. show the green emission from ZnO nanoparticles is originated from surface states rather than defects in bulk [4]. Many authors attributed this green emission band to oxygen vacancies [5]. To reduce the surface defects and enhance the UV emission intensity, passivation of ZnO nanoparticles surface with SiO_2 and MgO have been widely investigated [6–7]. Very recently, it was observed that ZnO nanoparticles encapsulated in mesoporous silica showed excitation wavelength dependent photoluminescence (PL) [8]. Few reports are available in the literature on excitation wavelength dependent PL of ZnO [9–12]. Yu et al. showed that there is enhancement in the UV emission with increase in excitation wavelength in pristine ZnO and ZnO coated with MgO nanowires [10]. They have also reported that UV emission can be excited effectively by the energies near the band gap. Djurisic et al. reported that green and yellow emissions could be excited by excitation below the band edge, while the orange–red emission could be by the excitation above the band edge [11]. Zeng et al. results infer blue emission can be excited near or less than the band gap energies, while the green emission can be excited at energies larger than band gap [12]. In the view of the existing literature, the excitation dependent PL behavior needs to be addressed further.

In this paper, ZnO nanoparticles were prepared by using poly (vinyl alcohol) (PVA). ZnO nanoparticles prepared in this study exhibited excitation wavelength dependent PL. The intensity of the UV emission is optimized by changing the excitation wavelength and the results were discussed.

2. Experimental procedures

The preparation of ZnO nanoparticles using PVA is as follows: $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in minimum quantity of de-ionized water and stirred for half an hour to get a homogeneous cationic solution. The metal nitrate to polymer (PVA) ratio is maintained as 1:3. Required quantity of PVA was added slowly into de-ionized water to obtain transparent and clear solution. Subsequently, the cationic solution was mixed with PVA solution under constant stirring and heating. The stirring and heating were continued until the gel like compound was formed. This gel type sample was dried at 150 °C for about 12 h in an oven to obtain black powder. Finally, samples were calcined in a programmable furnace at 600 °C at a rate of 2 °C/min and kept at that temperature for 1 h to get ZnO nanoparticles.

The structure and morphology of the samples are studied by an X-ray diffractometer (XRD) equipped with Cu K_α radiation and

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http://dx.doi.org/10.1016/j.matlet.2013.02.079

a Field Emission Scanning Electron Microscope (FE-SEM). The absorption properties of the samples are investigated by UV–vis absorption spectrometer (UV–vis). The PL and PL Excitation (PLE) spectra are acquired with a Xenon lamp of 450 W on a PL spectrometer.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction pattern of ZnO nanoparticles. The characteristic diffraction peaks corresponding to the reflection planes (100), (002), (101), (102), (110), (103) and (200) confirmed the hexagonal wurtzite structure of ZnO nanoparticles. The particle size of the ZnO nanoparticles has been calculated by using Debye–Scherrer's formula [13]. The calculated average particle size comes out to be 54 nm. Fig. 1(b) depicts the FE-SEM micrograph of the ZnO nanoparticles. The particle size calculated from this picture is 58 nm which is very close to the particle size obtained from XRD data. The purity of the sample was also tested with the help of the EDS measurement on FE-SEM and presented in Fig. 1(c). No foreign elements were detected in the EDS spectrum of the ZnO. The absorption spectrum of ZnO can also be seen in Fig. 1(d). The absorption peak is located at 377 nm, which exhibited a blue shift of 10 nm compared to the absorption peak of bulk ZnO which is positioned at 387 nm [13]. Obviously, this shift is due to the quantum confinement effects of ZnO nanoparticles.

The photoluminescence (PL) spectrum of ZnO nanoparticles recorded at an excitation wavelength of 320 nm is shown in Fig. 2(a). The substrate which has been used to hold the sample during the measurement exhibited a sharp emission peak at 420 nm. Deep analysis was made by fitting the curves by the Gaussian function. The Gaussian fitted PL spectrum shown in Fig. 2(b) composed of five peaks positioned at 398 nm, 418 nm, 434 nm, 467 nm and 492 nm. The familiar green emission (500–530 nm) which is mainly attributed to singly ionized oxygen vacancies by many authors is not observed in this study [4]. The absence of green emission implies that the sample would be rich in oxygen. The oxygen required to compensate the singly ionized oxygen vacancies that are responsible for the green emission could be supplied by the nitrates and PVA during the combustion. The emission peak at 398 nm was believed to have originated from the electron transition from the localized level slightly below conduction band to the valence band [14]. Some authors have also reported emission around 398 nm as near band edge emission [10,16]. The emission peaks at 418 nm and 437 nm have been attributed to the zinc vacancy related defect states [13,15]. Other visible emission peaks at 466 nm and 492 nm have been assigned to various deep level defect states originating from the zinc interstitials and/or oxygen vacancies [13,5].

Further, PL spectra were acquired at excitation wavelengths 300, 320, 340, 353 and 370 nm. For the sake of clarity, the PL spectra acquired with excitation wavelengths 300 nm and 370 nm are not shown (Fig. 3(a)). Similar spectra were obtained when excited with 300 nm and 320 nm excitation wavelengths. But when the excitation wavelength was changed to 340 nm, a sharp emission peak positioned at 384 nm with improved intensity compared to PL spectra obtained with 300 and 320 nm is observed along with other peaks. Obviously the emission at 384 nm is the near band edge emission. So it can be concluded that the emission at 398 nm originated due to the electron transition from the localized level slightly below conduction band to the valence band. Fig. 3(b) shows the PL excitation (PLE) spectrum of the ZnO nanoparticles. The PLE spectrum shows a

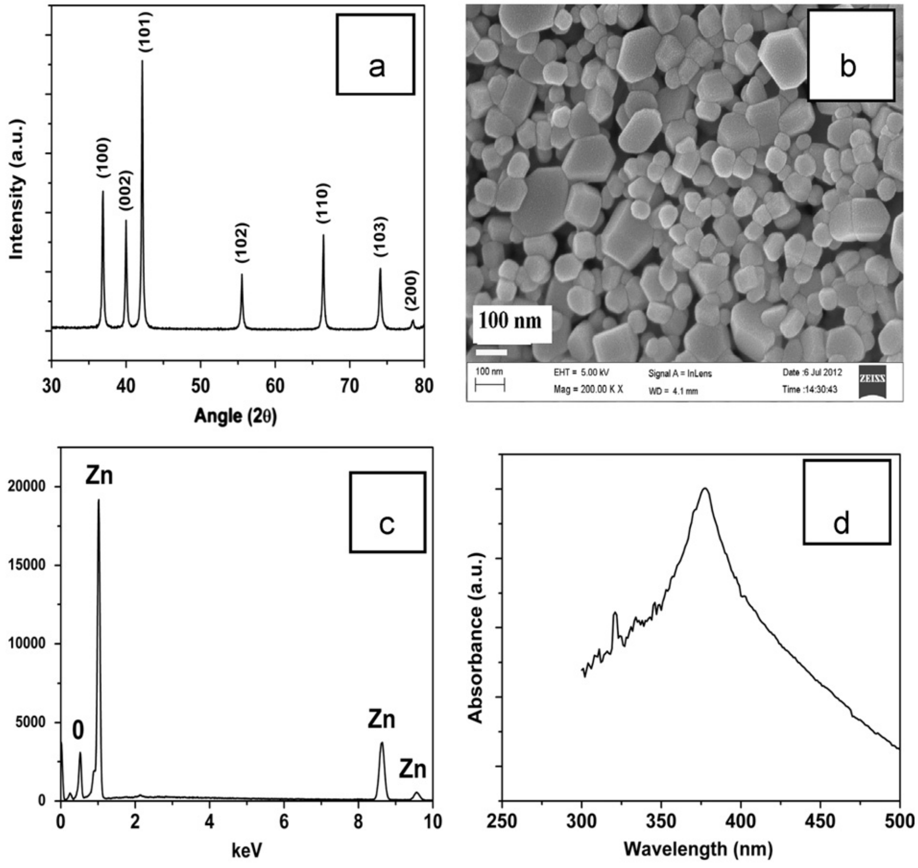

Fig. 1. The X-ray diffraction pattern (a), FE-SEM micrograph (b), EDS spectrum (c) and UV–vis absorption spectrum (d) of ZnO nanoparticles.

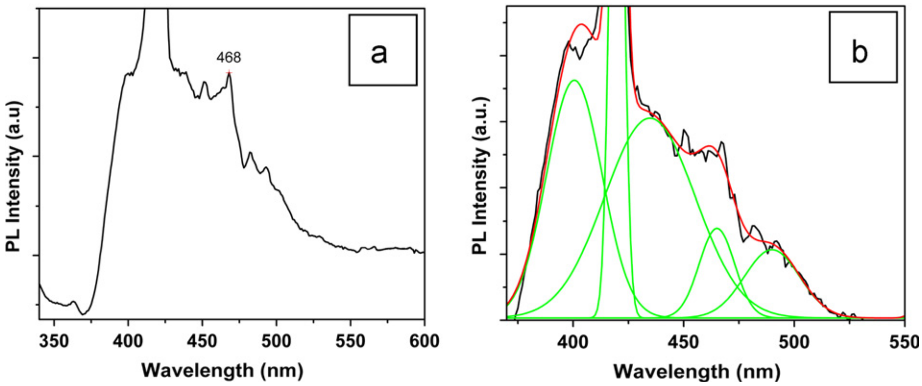

Fig. 2. PL spectrum of ZnO nanoparticles recorded with an excitation wavelength of 320 nm (a), and Gaussian fitted PL spectrum of ZnO nanoparticles (b).

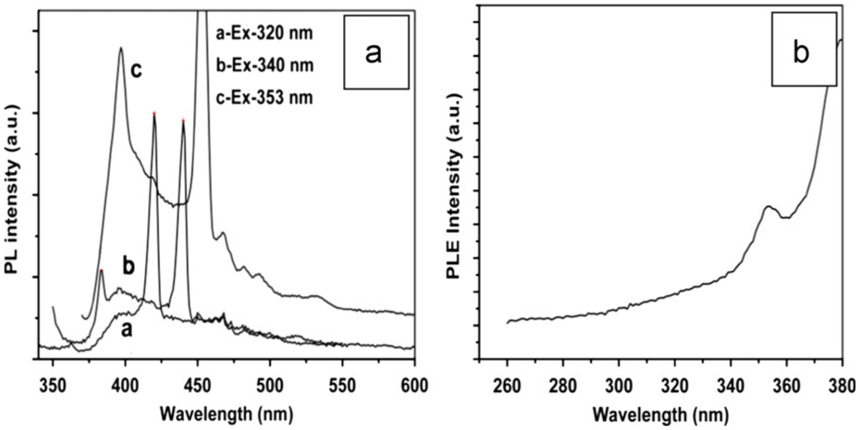

Fig. 3. PL spectra of ZnO nanoparticles taken at excitation wavelengths 340 nm and 353 nm (a) and PLE spectrum of ZnO acquired by monitoring the emission wavelength at 390 nm (b).

peak at 353 nm which corresponds to the excitation from valance band to the conduction band of ZnO semiconductor. When the excitation wavelength was fixed to 353 nm, the intensity of the 398 nm emission peak is raised to a value which is more than 23 times higher than the intensity of the 384 nm emission peak. For 370 nm excitation wavelength, the intensity of UV emission disappears. Recently Yu et al. reported that UV emission could be excited more effectively by energies near the band gap energies. Our results in this study show that the maximum UV intensity can be achieved only when the excitation wavelength is chosen from the PLE spectrum. There are drastic changes in the PL above and below this excitation wavelength. It can also be inferred from these results that there is no change in the position of the peaks with change in the excitation wavelength.

4. Conclusion

ZnO nanoparticles were prepared and the behavior of their PL with change in excitation wavelength was studied. There is no change in the PL for excitation wavelengths 300 and 320 nm when the excitation wavelength is fixed at 340 nm; PL spectrum shows another emission peak at 384 nm along with 398, 418, 434, 467 and 492 nm emissions. These results confirmed that the emission at 398 nm is not the band edge emission. But when the excitation wavelength was fixed at 353 nm, the band edge emission at 384 nm disappeared and the intensity of 398 nm emission was raised to 23 times that of its previous value. At 370 nm excitation wavelength, UV emission was quenched.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2013.02.079.

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