Journal of Luminescence 195 (2018) 201–208

Contents lists available at ScienceDirect

Journal of Luminescence

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

Oxygen vacancy mediated temperature dependent emission behavior of localized bound excitons in ZnO nanorods

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ARTICLE INFO

Keywords:
Oxygen vacancies defects
Bound excitons
Photoluminescence
ZnO nanorods

ABSTRACT

The present work reports on the tunable optical emission from oxygen vacancies in ZnO nanorods. The common green luminescence at room temperature originated from oxygen vacancy defects can be mediated by simply controlling pH values of alkaline solutions without the introduction of any intentional dopants. The peak energies of the green band are found to be monotonously tuned in the range from 2.17 to 2.47 eV, which could promote the applications of tunable wavelength ZnO optoelectronic devices. The temperature dependent behavior of exciton transitions and oxygen vacancy recombinations in ZnO nanorods is investigated in detail. It is suggested that the localized bound exciton (LBX) attached near the lateral facets of ZnO nanorods could survive up to nearly room temperature due to the large binding energy.

1. Introduction

In recent years, ZnO has attracted increasing attention in view of its direct wide band gap (3.37 eV) and large free exciton (FX) binding energy (approximately 60 meV). Wurtzite ZnO has been of considerable significance for the promising device applications such as short wavelength light emission diodes (LED), surface acoustic wave devices, transparent electrodes and so on [1,2]. One-dimensional (1D) ZnO nanostructures with diversified morphology such as nanotubes, nanowires, nanobelts, and nanorods have been studied widely which can be used as potential building block in nanoelectronic and nanooptoelectronic devices [3–6]. Specifically, ZnO nanorods in the form of hybrid or heterojunctions have shown extraordinary application prospects for photodetectors, gas sensors and photovoltaic devices in recent reports [7–10].

A photoluminescence (PL) spectroscope is a nondestructive and sensitive tool to investigate the native point defects in ZnO which are usually assumed to be responsible for the ubiquitous broad visible emission. The native point defects such as oxygen vacancies (V_O), oxygen interstitials (O_i), zinc vacancies (V_{Zn}), zinc interstitials (Zn_i) and oxide antisites (O_{Zn}) are suggested as candidates responsible for the origin of the omnipresent green luminescence band in ZnO PL spectra [11]. Although the exact structural origin of the green band remains controversial, V_O recombination is convincingly accepted by many researchers [12–14]. The peak positions and brightness of the green luminescence in ZnO can be varied by doping with different atoms, suitable for practical applications in light emission devices [15–18].

Besides visible emission, high crystalline quality ZnO thin films and nanomaterials usually exhibit UV emission. The near band edge (NBE) free excitons (FX), some bound excitons (BX) and donor-acceptor-pair (DAP) are usually concluded as origin of UV emissions in temperature dependent ZnO PL spectra [19,20]. In the present work, the modulation of V_O in ZnO nanorods was achieved by readily varying pH values in aqueous solutions without the introduction of any doping, which would result in the monotonous shift of the green band. In addition, the temperature behavior investigation on the exciton transitions and V_O recombinations is carried out.

2. Experiment

High purity anhydrous zinc acetate [$Zn(CH_3COO)_2$, $Zn(Ac)_2$] and ammonia were used without further purification for the undoped ZnO nanorods synthesis. In a typical synthesis, an aqueous solution containing adequate quantity of $Zn(Ac)_2$ was prepared and then dripped into the ammonia to regulate the solution pH as 8.5, 9, 9.5, 10 and 10.5, respectively. The resulting suspension was transferred into a stainless autoclave, and held at 140 °C for 24 h. The nanorods products were obtained by carefully filtering and washing the precipitates with deionized water.

The size and morphology of ZnO nanorods were measured by using a JSM-6700F field-emission scanning electron microscope (FE-SEM) and a JEOL2010 high resolution transmission electron microscope

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https://doi.org/10.1016/j.jlumin.2017.11.036
Received 21 July 2017; Received in revised form 19 November 2017; Accepted 21 November 2017
Available online 22 November 2017
0022-2313/

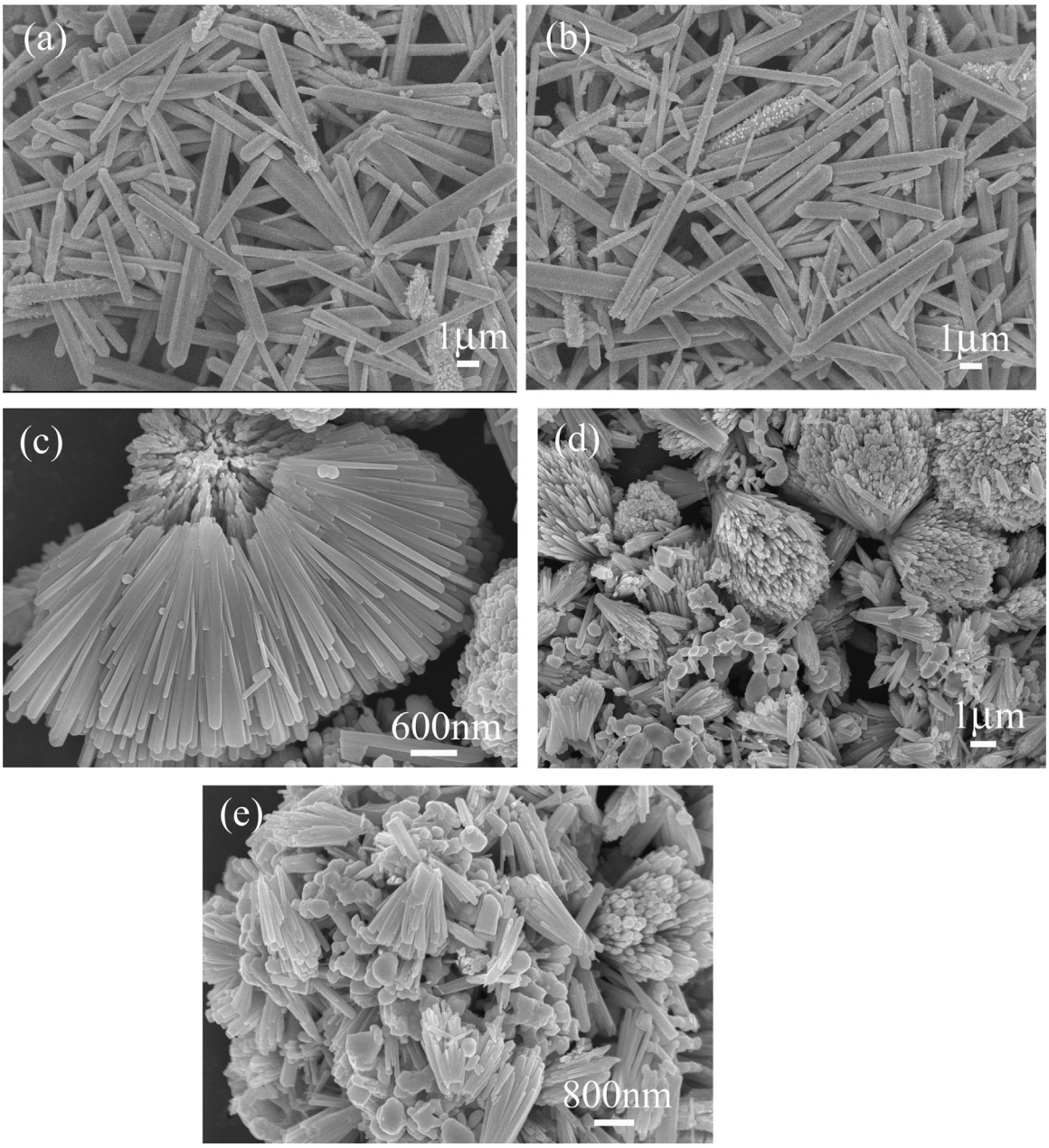

Fig. 1. FE-SEM images of ZnO nanorods prepared at different pH: (a) 8.5; (b) 9; (c) 9.5; (d) 10; (e) 10.5.

(HRTEM). The UV–Visible diffuse-reflectance spectra (Shimadzu, UV-2600) were measured for evaluating the optical absorption property of ZnO nanorods. X-ray photoelectron spectra (XPS) measurements were carried out with a Thermo-VG Escalab 250 X-ray photoelectron spectrometer. Temperature dependent PL spectra were performed using a He-Cd laser with an excitation wavelength of 325 nm.

3. Results and discussion

The typical FE-SEM images of ZnO nanorods prepared at different pH values are shown in Fig. 1. All ZnO samples exhibit rod-like shapes. ZnO nanorods for pH 8.5 and 9 are thick and long with an average diameter of 500 nm and an average length of 8 μm, while the samples for pH 9.5, 10 and 10.5 are relatively thin, short and fascicular with an average diameter of 200 nm and an average length of 3 μm. It is worth noting that there are many block and sphere-like structures distributed between the clusters of nanorods for pH 9.5, 10 and 10.5. The nanorods structure is further investigated using a selected area diffraction pattern (SAED) and HRTEM. Fig. 2(b) presents a SAED pattern taken from a single nanorod (Fig. 2(a)) prepared at pH 8.5, which indicates that ZnO nanorods are single crystalline and the growth direction is along the [11$\bar{2}$0] direction. Fig. 2(c) shows an HRTEM image recorded on the single nanorod revealing that ZnO nanorods are basically layer-structured with a layer spacing of 0.51 nm, corresponding to the d-spacing of (0001) planes as reported in the literature [21,22]. It can be also seen from Fig. 2(c) that there exists a lot of basal plane stacking faults in the lateral facets which can trap electro-hole pairs to create LBX contributing to UV emission as shown in the PL spectra later. The basal plane stacking faults for samples grown at pH 9, 9.5, 10 and 10.5 can also be clearly observed in the lateral facets of nanorods as shown in Fig. 3.

The effect of pH values on the optical absorption property of ZnO nanorods was evaluated by the UV–Visible diffuse-reflectance spectra. As can be seen from Fig. 4 plotted in normalized scale, the absorption edges of ZnO nanorods prepared at different pH values are 408, 408, 403, 397 and 392 nm, respectively, corresponding to the optical band