Enhancement of nonlinear optical phenomena from crown-like nanostructure zinc oxide based on whispering gallery mode*

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Whispering gallery mode (WGM)-enhanced nonlinear optical phenomena from crown-like nanostructure zinc oxide (ZnO) samples are observed. The samples are synthesized by vapor-phase transport method. The morphology and crystal structure are examined and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM), and they are excited by femtosecond laser pulses with central wavelengths of 355 nm, 800 nm and 1150 nm, respectively. The typical stimulated emission presents a red shift compared with spontaneous emission, which is observed under the excitation of 355 nm with a relatively low threshold. The ultraviolet (UV) frequency up-conversion emission is obtained when the excitation pulse wavelengths are selected as 800 nm and 1150 nm, respectively. The peak position and the relationship between the emission intensity and excitation intensity demonstrate that the UV up-conversion photoluminescence (PL) is induced by two- and three-photon absorptions. The PL characteristics and their WGM-enhanced mechanism are investigated.

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Zinc oxide (ZnO) has three fast growth directions of [0001], $[10\bar{1}0]$ and $[2\bar{1}\bar{1}0]$, which is easy for realizing many kinds of novel nanostructures with different morphologies to obtain fascinating photoluminescence (PL) characteristics and potential applications[1-5]. In recent years, the microcavities based on ZnO nanorods with hexagonal cross section or hexagonal nanodisks employing whispering gallery mode (WGM) resonators have attracted much interest because it is easier to obtain strong WGM-enhanced emission with relatively low exciting conditions[6-9]. In addition, optical nonlinearity effects, such as the second and the third harmonic generations, two-photon absorption and corresponding PL, have been found in ZnO thin film and nanowires. All these nonlinear effects have shown the potential applications in optical limiting, all-optical switching and optical data storage. It has been forecasted that based on WGM-enhanced effects, more efficient optical nonlinearity can be observed in two- or three-dimensional nanostructure ZnO samples. In other words, WGM-enhanced effect can make optical nonlinearity easy to be obtained in WGM resonators (WGMRs).

In this paper, the crown-like nanostructure ZnO composed of a hexagonal cap and a tower-like shaft is synthesized by vapor-phase transport method. Its morphology and crystal structure are examined and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Under the excitation of pulse laser with central wavelengths of 355 nm, 800 nm and 1150 nm, the stimulated emission and strong ultraviolet (UV) multi-photon induced PL are observed.

The ZnO samples were prepared with a vapor-phase transport method described in Ref.[8]. After examining the morphology and characteristics, several individual samples with suitable morphology and good crystal structure were selected for the investigation of PL characteristics. Firstly, the sample was excited by a frequency-tripled Nd:YAG laser at pulsed operation with wavelength of 355 nm, full width at half maximum (FWHM) of 6 nm and repetition frequency of 10 Hz. Then a Ti: sapphire laser operating from 800 nm to 1100 nm for femtosecond pulse, which is generated from an optical parametric oscillator, was used as the excitation light source in application. The repetition frequency was 1000 Hz, and the pulse duration was 150 fs. All the excitation beams were focused onto a spot by a convex lens with the diameter of about 100 μm, and the emission signal was recorded by a fiber-coupled optical multi-channel analyzer (OMA). All the measurements were carried out

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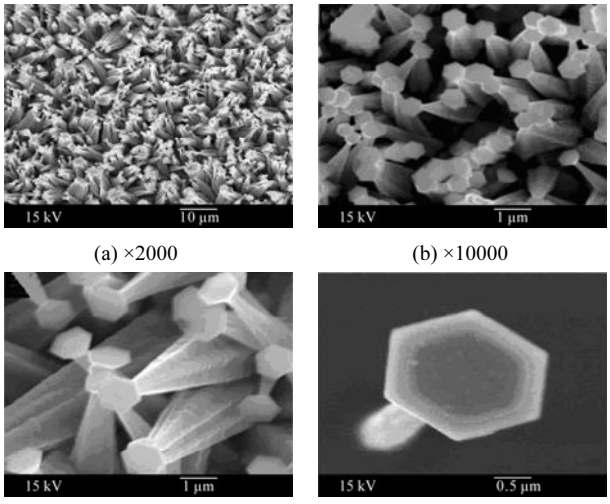
at room temperature.

The SEM analyses shown in Fig.1 illustrate that each product presents a crown-like morphology composed of two parts, which are a tower-like shaft with various diameter from several micrometers to several hundred nanometers from the bottom to the top, and a hexagonal disk with diameter about 1μm caping on the shaft top. Fig.1(d) shows the field emission SEM image of a selected product, and a dark hexagonal spot can be obviously seen on the disk-like cap.

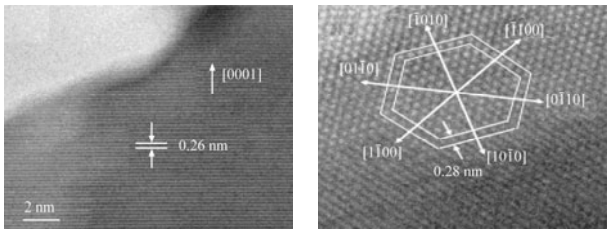


(a) ×2000 (b) ×10000

(c) ×15000 (d) ×30000

Fig.1 SEM images of the crown-like ZnO samples with different magnifications

The HRTEM images and XRD pattern of the crown-like ZnO sample are illustrated in Figs.2 and 3, respectively. As the lattice fringes shown in Fig.2(a), i.e., the HRTEM image of the shaft, the 0.26 nm d-spacing matches the interspacing of [0001] of wurzite ZnO, which is consistent with the XRD pattern shown in Fig.3.



(a) Tower-like shaft (b) Disk-like cap

Fig.2 HRTEM images of the shaft and the disk-like cap of the crown-like ZnO sample

Fig.2(b) shows the HRTEM image of the disk-like cap observed along [0001] direction. It can be seen from this image that the atoms arrange regularly to form a six-fold symmetric projected structure. The 0.28 nm d-spacing between any two adjacent lattice fringes along six symmetric directions corresponds to the interspacing of $[10\bar{1}0]$ of wurtzite ZnO. This indicates that the disk-like cap is formed by [0001] plane closed by six symmetric $[10\bar{1}0]$.

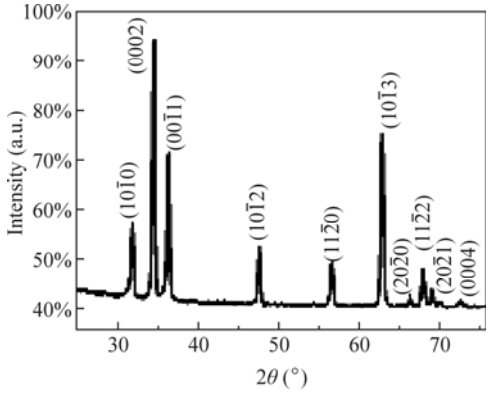
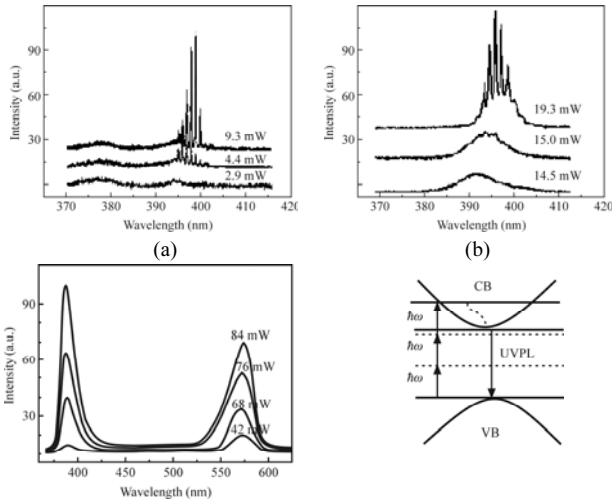


Fig.3 XRD pattern of the crown-like ZnO sample

When the excitation light irradiates the disk-like cap with the incident angle of about 60º to one side surface of the cap, vertical to the axis of the shaft, the emission spectra at different excitation power densities and wavelengths are obtained as shown in Fig.4(a)–(c).



(a) (b)

(c) (d)

Fig.4 PL spectra of crown-like ZnO samples under different excitation wavelengths of (a) 355 nm, (b) 800 nm, and (c) 1100 nm; (d) Schematic diagram of its band gap

Fig.4(a) gives the emission spectra and the variation with the increase of excitation power density for excitation light with wavelength of 355 nm. At low excitation power density of 2.9 mW, the spectrum shows a broad spontaneous emission band centered at about 393 nm, and the FWHM is about 5 nm. When the excitation power is increased to 4.4 mW, the discrete peaks merge in the spontaneous emission spectrum. When the excitation power is further increased to 9.3 mW, more discrete peaks with FWHM of about 0.3 nm appear in the range from 390 nm to 398 nm, and the peak intensity is increased more dramatically. The narrow width indicates a transition from the spontaneous emission to the stimulated emission. The multi-peak spectral structure reveals multiple lasing modes with the average mode spacing of 1.0 μm. These experimental results indicate that the disk-like cap works as a resonator, and the Q-factor of

this microcavity may be estimated at about 1300 according to the equation of $Q=\lambda/\Delta\lambda$, where λ and $\Delta\lambda$ are peak wavelength and FWMH, respectively. Generally, the output lasing generally contains both TM and TE polarizations. However, the intensity of TM polarized emission is much weaker than that of TE mode. Thus, it is reasonable to denote the TE mode to discuss the lasing behaviors. According to the equation of the plane wave model for the WGMR and the refractive index for TE mode described by the Sellmeier dispersion function[6,8] as

$$Q_{\mathrm{WGR}} = \frac{\pi r m n R^{m/4}}{\lambda(1-R^{m/2})}\sin(\frac{2\pi}{m}), \quad (1)$$

$$n_{\mathrm{TE}} = 1.9384 + 1.1775\times10^{-2}(h\nu)^2 + 1.5237\times10^{-3}(h\nu)^4, \quad (2)$$

where r is the diameter of the cap, R=15% is the reflectivity at ZnO/air boundary, n is the refractive index of TE mode, m is the mode number of the stimulated emission, h is the Planck constant, and ν is the frequency of the emission light, the Q-factor and mode numbers can be simulated. The simulated results are well consistent with the observed data. So the lasing modes illustrated in Fig.4(a) should be attributed to the WGMR based on the disk-like cap with hexagonal cross section, whose schematic diagrams are shown in Fig.5.

Fig.4(b) shows the PL spectra of the sample excited by 800 nm femtosecond laser with different power densities. When the excitation intensity is increased to be strong enough, discrete stimulated emission with FWHM about 0.3 nm is observed, which is similar to PL shown in Fig.4(a). Relationship between wavelengths of emission and exciting light means that the frequency up-conversion emission phenomena may originate from the two-photon absorption. So we calculate the relationship of UV emission intensity versus the square of the excitation power. The approximate linearity confirms our prediction. Compared with the similar two-photon induced stimulated emission of ZnO nanostructure from non-WGM cavity, our work has much lower threshold, which is also attributed to the WGM-enhanced effect.

Fig.4(c) shows the PL spectra of the sample excited by 1150 nm femtosecond laser with different power densities. It can be seen that all spectra contain a UV band with peak at 388 nm and a visible band centered at 575 nm. Because the excitation wavelength is more than three times of the peak wavelength, it is believed that the UV emission can be generated from three-photon induced photoluminescence (TPPL) process. The TPPL originates from the three-photon absorption. So according to the solution of the time dependent Schrödinger equation using the third-order perturbation theory[13], the TPPL mechanism in the case of our products can be explained as follows. An electron in the valence band (VB) simultaneously absorbs three photons by intermediate energy bands, transits to the conduction band (CB), then relaxes to an exciton state near the band edge, and finally generates UV emission by exciton recombination, as shown in Fig.4(d).

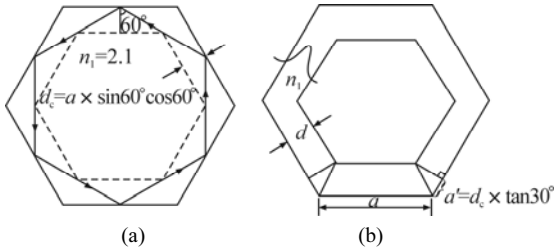


Fig.5 (a) Principle of WGMR with hexagonal cap cross section based on internal reflection; (b) Cross section of the designed WGMR

In an oscillator as shown in Fig.5, the light circulates with negligible loss due to the multiple total internal reflections at the resonator's boundary. Lower irradiation loss makes this kind of cavity with higher value of Q-factor, which is beneficial to the spontaneous emisson with low excitation intensty and the stimulated emission with low threshold. In addition, Wiersig et al[10] carried out a numerical analysis of long-lived modes in hexagonal dielectric resonant cavity, and showed that the intensity is concentrated near the boundary of the hexagonal resonator. The results are illustrated in Fig.6.

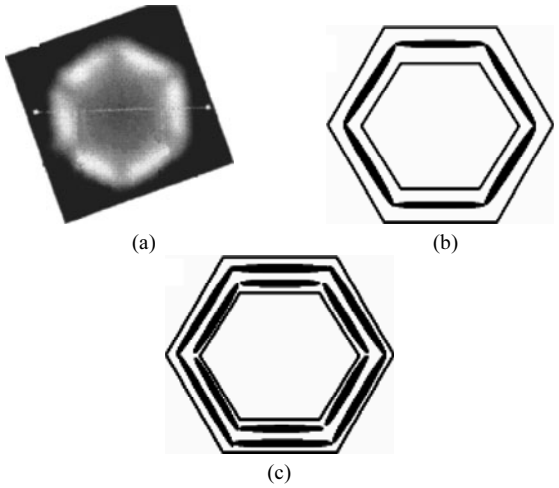


Fig.6 Simulation results of (a) optical field distribution in WGMR, (b) envelop of foundation mode and (c) envelop of the first-order mode

As shown in Fig.6(a), the optical field intensity of a vertically oriented disk-like cap is not uniformly distributed across the cap, but it is locally concentrated near the hexagonal boundary. This type of spatial localization of optical field intensity is typically observed in a WGMR, and makes more intensive excitation light in this area. It is reasonable to consider that this location of optical field works as the source of WGM-enhanced emission[9]. It makes the emission from WGMR much stronger than that from one-dimensional nanostructures, such as nanowire and nanoscale thin film under the same excitation power level. Furthermore, compared with UV spontaneous emission at 383 nm from one-dimensional ZnO micro/nanostructures, the UV spontaneous emission from our sample has a red shift of about 9 nm for peak wavelength. Firstly, it should be attributed to band gap renormalization at

higher excitation power densities generated from the optical field localization in WGMR[5,6,8]. The reasons of all WGM-enhanced emission phenomena are the low radiation loss resulting from internal reflection and the localization of excitation energy near boundary in the WGMR. In other hand, the strong excitation power density near WGMR boundary resulting from the localization of optical field can raise the exciton concentration in gain medium. At this time, the emission from exciton-exciton inelastic collision can replace that from exciton recombination as the main source of PL in our samples. And the photo energy E_q is determined as[11,12]

$$E_q = E_{ex} - E_b^{ex}(1-1/q^2) - 3kT/2, \quad (3)$$

where E_{ex} is energy of exciton in excited state, q is the charge of electron, T is the absolute temperature, and k is the state quantum number of the free exciton after collision. According to Eq.(3), the energy of photon emitted from exciton-exciton collision is lower by about 84 meV than that from free exciton recombination, which is corresponding to about 9 nm red shift in wavelength.

This opinion is confirmed by that it is a linear relationship between the UV emission intensity and the cube of excitation power as shown in Fig.7.

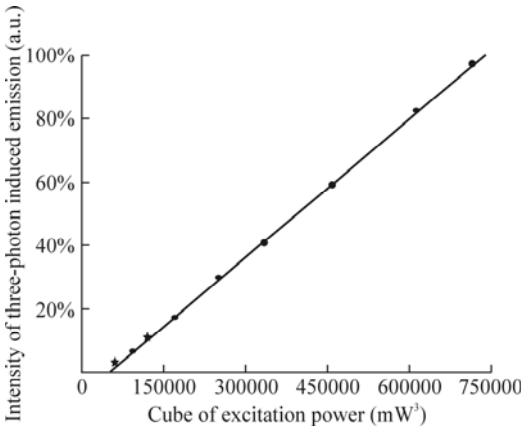


Fig.7 The three-photon induced UV emission intensity versus the cube of excitation power

According to the pulse duration, the repetition frequency of the laser and the size of excitation light spot, it can be calculated that the TPPL threshold is about 0.22 TW/cm^2, which is in the same order of magnitude with the threshold of two-photon absorption in ZnO nanowires reported in Ref.[14]. Considering that the efficiency of three-photon absorption is about one order of magnitude lower than that of two-photon absorption in the same material reported in Ref.[15], it is believed that our crown-like samples have higher three-photon absorption efficiency. This higher absorption efficiency partially should be ascribed to the contribution of localization of excitation light energy for WGM-enhanced effect in resonator. The disk-like cap and shaft structure of our samples can reduce the vertical radiation loss induced by the mode coupling between the WGM mode and vertical radiation mode in the pedestal, which is also beneficial to the excitation power enhancement in the gain area near the boundary of the WGMR[16].

In conclusion, the crown-like ZnO samples are prepared by vapor phase transport method. After their morphology and crystal structure are examined and characterized, they are excited by femtosecond laser pulses with central wavelengths of 355 nm, 800 nm and 1150 nm. The typical WGM stimulated emission, which has a red shift compared with spontaneous emission, two-photon induced stimulated emission and TTPL are observed with lower threshold compared with ZnO nanowires, nanorods and so on, which have uniform diameters. Theoretical analysis and numerical simulation indicate that these mentioned phenomena are all attributed to the WGM-enhanced effect. And in this paper, the WGM-enhanced effect is strengthened, because the cap and shaft structure reduce the radiation loss induced by the mode coupling loss between the WGM mode and vertical radiation mode in the shaft.

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