

# Negative Slope for Second Harmonic Generation Observed at High Excitation Intensities in ZnO Nanorods

Jun Dai, Qiao-Feng Dai, Jian-Hua Zeng, Sheng Lan, Xia Wan, and Shao-Long Tie

**Abstract**—The nonlinear optical properties of ZnO nanorods (NRs) synthesized by coprecipitation method were investigated using a focused femtosecond laser light. The excitation wavelength was tuned from 750 to 795 nm so that excitons could be selectively generated via two-photon absorption above or below the exciton ground state of ZnO NRs. Both second harmonic generation (SHG) and two-photon-induced luminescence (TPL) were observed in the nonlinear response spectrum of ZnO NRs. The relative intensities of SHG and TPL were found to depend not only on excitation wavelength, but also on excitation intensity. At high excitation intensities, the nonlinear response spectrum became dominated by TPL for excitation wavelengths shorter than 770 nm, whereas it was still governed by SHG for excitation wavelengths longer than 770 nm. In addition, the intensities of SHG and TPL did not scale quadratically with excitation intensity but exhibited different slopes in different excitation intensity regimes, implying the existence of competition between them. More interestingly, a negative slope, which indicates a reduction of SHG with increasing excitation intensity, was observed at high excitation intensities for excitation wavelengths longer than 770 nm, implying the energy redistribution or energy transfer between SHG and TPL. Meanwhile, a slope much  $>2.0$  was identified for TPL at high excitation intensities. It is suggested that the reduction in the bandgap energy resulting from the effects of bandgap renormalization and temperature rise were responsible for the rapid increase of TPL. A weak exciton emission was resolved for excitation wavelengths longer than 770 nm and it was explained by the existence of Rabi oscillation.

**Index Terms**—ZnO nanorods (NRs), second harmonic generation (SHG), two-photon-induced luminescence (TPL).

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## I. INTRODUCTION

As a wide bandgap semiconductor, wurtzite ZnO with exciton binding energy as large as 60 meV has attracted the attention of researchers for many years due to its potential applications in various fields of science and technology [1]–[6]. In recent years, much effort has been devoted to the fabrication and characterization of ZnO micro- and nanostructures, including nanorods (NRs) [7]–[9], nanowires [10]–[13], nanotubes [14], [15], nanoneedles [16], and nanobelts [17] etc. Apart from their linear optical properties, the nonlinear optical properties of these ZnO nanostructures have been extensively studied. Second harmonic generation (SHG) [13], [18], [21], [22], [24], [31], [32], two-photon-induced luminescence (TPL) [19], [20], [31], [32] and even multiphoton-induced photoluminescence (MPL) [21], [24], [25] have been observed by exciting these ZnO nanostructures with femtosecond (fs) lasers possessing high peak powers. While SHG is generally observed at the half wavelength of the excitation wavelength, TPL or MPL usually involves the emissions from the exciton states and/or various defects levels present in ZnO nanostructures. The most commonly observed MPL is the broad green emission band which has been ascribed to the emission from the defect levels of oxygen vacancies. In experiments, resonance enhancement of SHG was observed in ZnO nanowires when the excitation wavelength was tuned to the exciton energy, indicating the energy transfer from TPL to SHG [22]. In addition, the maximum TPL was observed when the excitation wavelength corresponding to the bandgap energy by two-photon absorption (TPA) was employed [17].

Although the dependence of SHG and MPL intensities on excitation wavelength and intensity has been investigated for various ZnO nanostructures [17], [21], [24]–[26], [31], [32], very few work has been carried out to address the competition or energy exchange between these nonlinear processes which take place simultaneously under fs laser excitation. Since the orders of these nonlinear processes and the responses of them to the excitation of fs lasers are different, it is expected that the competition or energy exchange between them will strongly depend on excitation wavelength and excitation intensity. Recently, the saturation of the SHG from GaAs-filled metallic hole arrays has been observed and it was ascribed to three-photon absorption and the resultant free-carrier absorption [23]. A decrease of SHG with increasing excitation intensity was also predicted at high excitation intensities when three-photon absorption and the resultant free carrier absorption were taken into account [23]. It means that

SHG may be depleted through various channels. However, this theoretical prediction was not confirmed due to the required high excitation intensity which may exceed the damage threshold of the material. In the fs laser ablation of materials, the creation of high spatial frequency periodic surface structures on the surface of ZnO films has been ascribed to the intense SHG induced by fs laser pulses on the surface [27]. In this case, it was suggested that the SHG was effectively absorbed by ZnO films. Therefore, the investigation of the excitation wavelength and intensity dependent competition and energy transfer between these nonlinear processes is not only interesting for fundamental research but also important for practical application.

## II. SAMPLE PREPARATION AND EXPERIMENTAL SCHEME

The ZnO NRs used in our study were synthesized by using the method reported previously [28]. The synthesis process for ZnO NRs can be described in three steps. First, 250-mL aqueous solutions of zinc acetate ( $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$ ) and triethanolamine (TEA,  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ ) with molar ratio of 1:2 were prepared and put inside two dropping funnels. Then, the two solutions were dropped within 2 hours into a three-neck flask filled with water and subjected to a bath at 90 °C. Subsequently, the above suspension was continuously stirred for 1 hour. Finally, the suspension containing ZnO seeds was aged for 12 hours at room temperature. After filtration, the residue was washed three times with acidic and deionized water and dried at 80 °C for 24 hours to obtain ZnO NRs. The scanning electron microscope images of the as-prepared ZnO NRs can be found in our previous publications [29], [30]. The average diameter and length of ZnO NRs were measured to be  $\sim 200$  nm and  $\sim 2$   $\mu\text{m}$ , respectively.

For the measurements of SHG and TPL, ZnO NRs were densely compressed into a 100- $\mu\text{m}$ -thick film. The fs laser light (120 fs; 76 MHz) from a Ti : sapphire oscillator (Mira 900, Coherent) was introduced into an inverted microscope (Axio Observer A1, Zeiss) and focused on the sample by using a 40 $\times$  objective lens with NA = 0.65. The nonlinear optical signals from ZnO NRs were collected by using the same objective lens and delivered to the combination of a spectrometer (SR-500I-B1, Andor) and a CCD (DU970N, Andor) for spectrum analysis.

The excitation wavelength was tuned from 750 to 795 nm so that the efficiency of exciton generation via TPA can be varied. Following TPA, TPL can be generated through the radiative recombination of excitons at low excitation intensities or electron-hole plasma at high excitation intensities. Meanwhile, SHG can be produced coherently without the generation of excitons. Therefore, the energy levels of ZnO NRs provide an ideal platform to examine the competition between SHG and TPL by adjusting excitation wavelength or varying excitation intensity.

## III. RESULTS AND DISCUSSION

### A. Nonlinear Response Spectra of ZnO NRs at Different Excitation Wavelengths

In experiments, we measured the nonlinear response spectra of ZnO NRs at different excitation wavelengths ( $\lambda_{\text{ex}}$ )

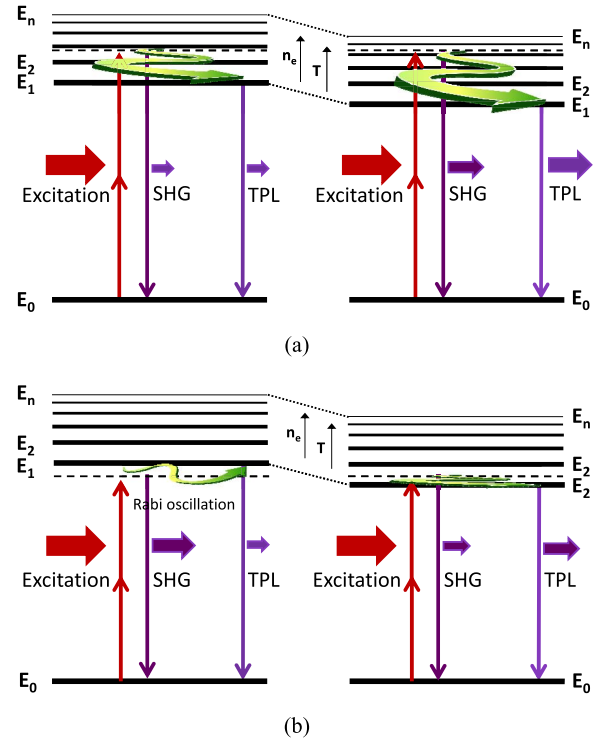


Fig. 1. Nonlinear optical processes occurring in ZnO NRs under the excitation of fs laser pulses with wavelengths shorter (a) and longer (b) than 770 nm. In both cases, a reduction in the bandgap (or exciton) energy is expected with increasing excitation intensity due to the effects of bandgap renormalization and temperature rise which are indicated by the increase in carrier density ( $n_e$ ) and temperature ( $T$ ). (a)  $\lambda_{\text{ex}} \leq 770$  nm. (b)  $\lambda_{\text{ex}} > 770$  nm.

ranging from 750 to 795 nm. For each excitation wavelength, the excitation intensity dependent nonlinear response spectrum was carefully measured. The nonlinear optical processes occurring in ZnO NRs under the excitation of fs laser pulses are schematically depicted in Fig. 1. As compared to the energy of the exciton ground state in ZnO, the energy of two photons is larger for excitation wavelengths shorter than 770 nm. In this case, the excitation of excitons into the exciton states through TPA is possible, as shown in Fig. 1(a). For excitation wavelengths longer than 770 nm, one can only expect the excitation of excitons into the exciton ground state through TPA with Rabi oscillation [32] or through three-photon absorption with a much smaller absorption coefficient, as shown in Fig. 1(b). At low excitation intensities, TPL is expected to be comparable with SHG in the former case because it involves the generation of excitons. In comparison, the latter case is thought to be dominated by SHG because the possibility of exciton generation is quite small. At high excitation intensities, a reduction in the bandgap energy of ZnO is expected due to the effects of bandgap renormalization and temperature rise, as schematically shown in Fig. 1. Consequently, more excitons will be generated in both cases, leading to a dramatic increase in TPL. Therefore, the competition between SHG and TPL will be manifested in both the excitation wavelength and the excitation intensity dependent nonlinear responses of ZnO NRs which will be described in the following.

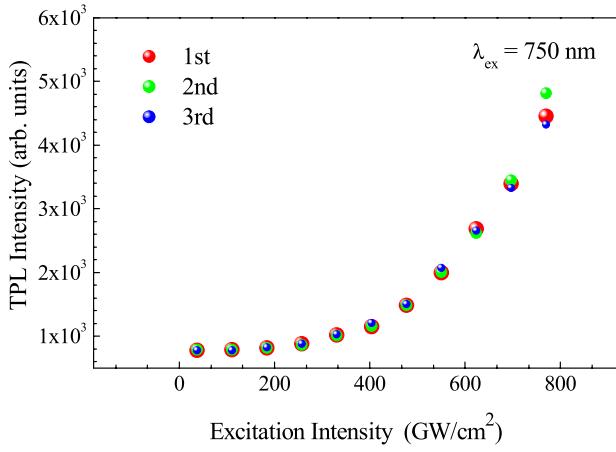


Fig. 2. Excitation intensity dependent TPL measured in three different rounds.

In order to ensure that no damage or ablation of ZnO NRs occurred at high excitation intensities, the maximum excitation intensity was restricted to be lower than  $770 \text{ GW/cm}^2$ . Under this condition, the excitation intensity dependent measurements for TPL could be well repeated, as shown in Fig. 2 for  $\lambda_{\text{ex}} = 750 \text{ nm}$  at which the strongest TPA was expected.

The excitation intensity dependent nonlinear response spectra obtained at different excitation wavelengths are shown in Fig. 3. In all spectra, one can clearly identify the SHG and TPL emission peaks at high excitation intensities. The TPL include the emissions from excitons and electron-hole plasma. The exciton emission, which is located at  $\sim 380 \text{ nm}$ , can only be resolved for excitation wavelengths longer than  $770 \text{ nm}$ , as indicated by the arrows in Fig. 3. For excitation wavelengths shorter than  $770 \text{ nm}$ , the exciton emission cannot be clearly resolved because its intensity is quite weak as compared to that of the SHG. The strong emission observed at the long-wavelength side of the exciton emission is ascribed to the radiative recombination of electron-hole plasma which dominates the TPL at high excitation intensities when the density of excitons exceed the Mott density [33]. In Fig. 3, a redshift of the TPL is also observed with increasing excitation intensity. Previously, the nonlinear optical properties of other ZnO nanostructures, such as nanowires and nanobelts [18]–[22], [24], [25], [31], [32], have been studied by using a fs laser. Except the exciton emission appearing at  $\sim 380 \text{ nm}$ , a broad emission band centered at  $\sim 530 \text{ nm}$  was usually observed. It was ascribed to the emission from the defect levels of oxygen vacancies induced in the fabrication of ZnO nanostructures. In our case, the intensity of the green emission band is quite weak as compared to the violet emission band at  $\sim 410 \text{ nm}$ , especially at high excitation intensities. Although both SHG and TPL could be observed at high excitation intensities for all excitation wavelengths, it can be seen that the nonlinear spectrum is dominated by TPL for excitation wavelengths shorter than  $770 \text{ nm}$  while it is governed by SHG for excitation wavelengths longer than  $770 \text{ nm}$ .

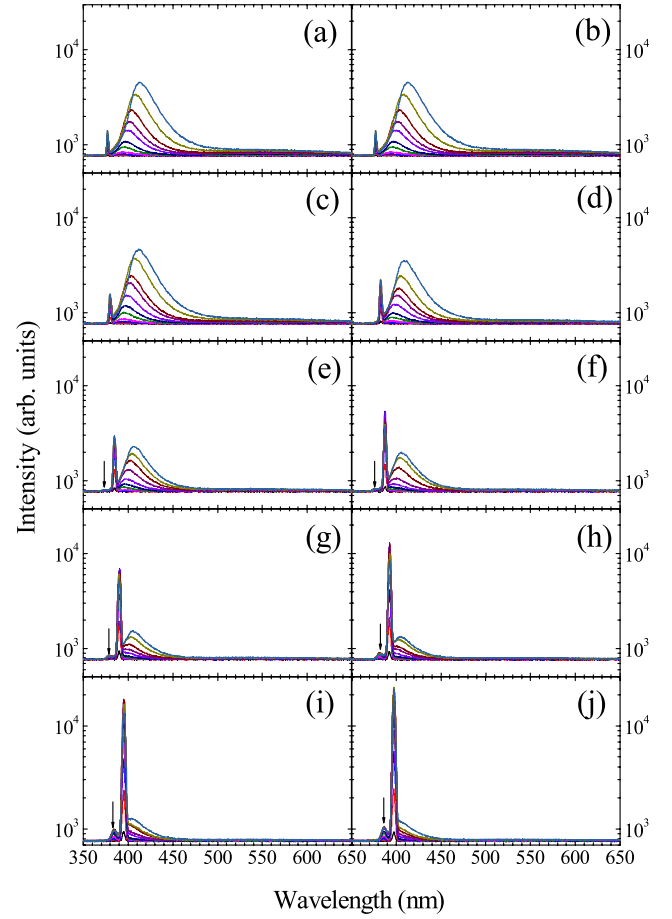


Fig. 3. Evolution of the nonlinear response spectrum of ZnO NRs with increasing excitation intensity measured at different excitation wavelengths. (a)  $\lambda_{\text{ex}} = 750 \text{ nm}$ . (b)  $\lambda_{\text{ex}} = 755 \text{ nm}$ . (c)  $\lambda_{\text{ex}} = 760 \text{ nm}$ . (d)  $\lambda_{\text{ex}} = 765 \text{ nm}$ . (e)  $\lambda_{\text{ex}} = 770 \text{ nm}$ . (f)  $\lambda_{\text{ex}} = 775 \text{ nm}$ . (g)  $\lambda_{\text{ex}} = 780 \text{ nm}$ . (h)  $\lambda_{\text{ex}} = 785 \text{ nm}$ . (i)  $\lambda_{\text{ex}} = 790 \text{ nm}$ . (j)  $\lambda_{\text{ex}} = 795 \text{ nm}$ .

### B. Excitation Intensity Dependent SHG and TPL Measured at Different Excitation Wavelengths

In Fig. 4, we summarized the excitation intensity dependent SHG and TPL (consider only the emission of electron-hole plasma) at different excitation wavelengths and provided the fittings for the experimental data. In all cases, the excitation intensity dependent nonlinear signals (SHG or TPL) can be classified into two regimes in which they exhibit different dependences on excitation intensity, as indicated by the straight lines with different slopes. In addition, the excitation intensities at which the transition from one slope to the other were found to be different for SHG and TPL. The transition excitation intensity for SHG appeared to be larger than that for TPL. Furthermore, the slope for SHG decreases rapidly while that for TPL increases dramatically with increasing excitation intensity. This phenomenon clearly indicates the existence of competition between SHG and TPL.

In order to show more clearly the competition and energy transfer between SHG and TPL, we present the excitation intensity dependent SHG and TPL measured at  $765 \text{ nm}$  in a linear coordinate, as shown in Fig. 5. A gradual saturation of SHG and a rapid increase in TPL are observed at high excitation intensities. At an excitation intensity of  $\sim 650 \text{ GW/cm}^2$ ,

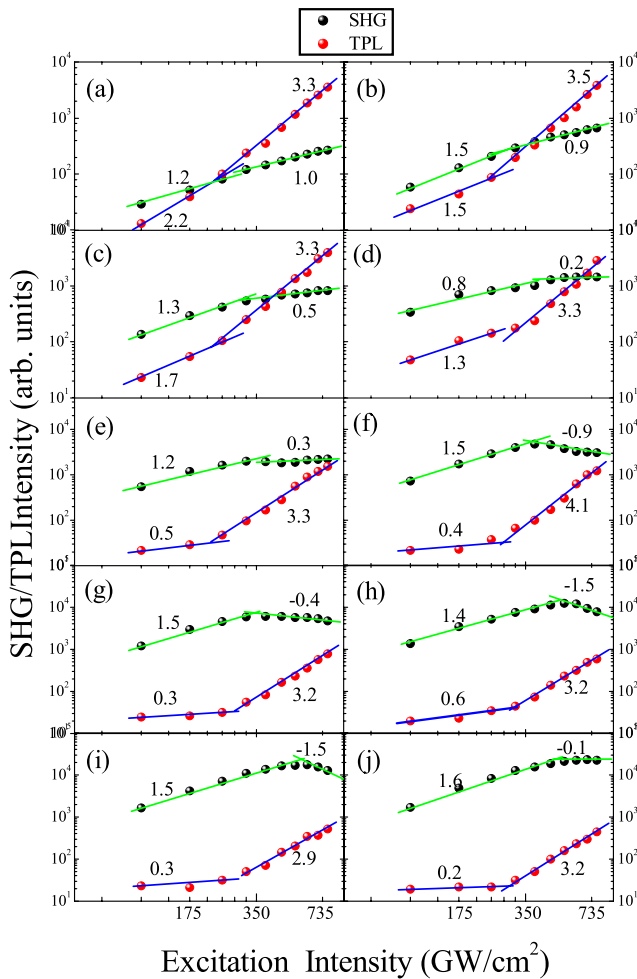


Fig. 4. Excitation intensity dependent SHG and TPL observed at different excitation wavelengths. In each case, the slopes of SHG and TPL are provided for the low and high excitation intensity regimes. (a) 750 nm. (b) 755 nm. (c) 760 nm. (d) 765 nm. (e) 770 nm. (f) 775 nm. (g) 780 nm. (h) 785 nm. (i) 790 nm. (j) 795 nm.

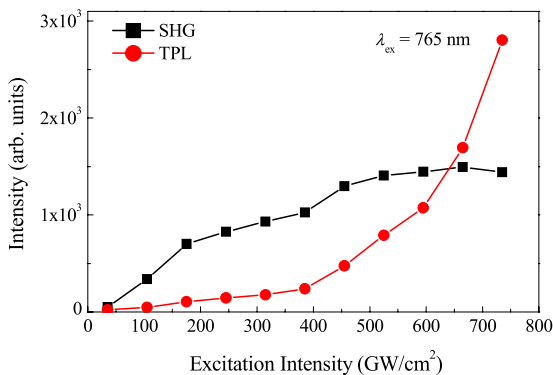


Fig. 5. Excitation intensity dependent SHG and TPL plotted in a linear coordinate. A gradual saturation of SHG and a rapid increase in TPL are observed, indicating the existence of competition between them.

the intensity of TPL becomes equal to that of SHG. After that, the nonlinear response is dominated by TPL.

Now let us examine carefully the excitation wavelength and intensity dependent SHG and TPL summarized in Fig. 4. For clarity, we present the dependences of the slopes for

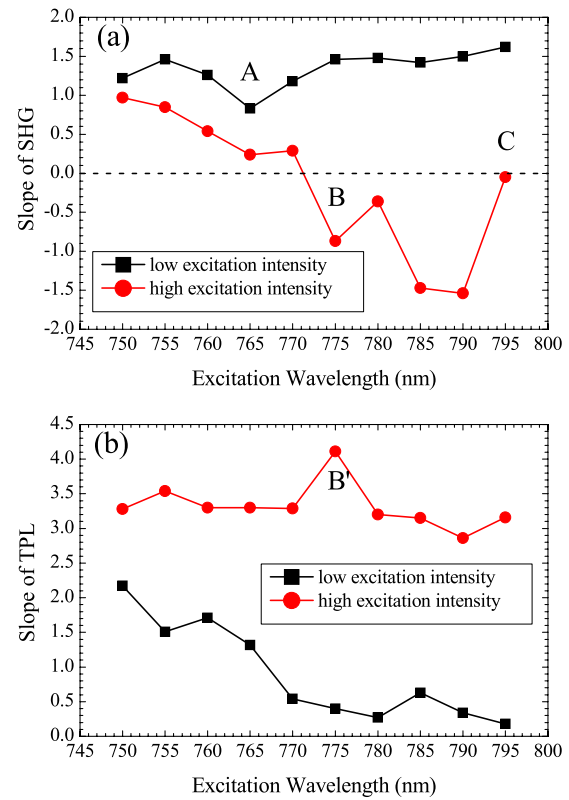


Fig. 6. Dependence of the slope of SHG (a) and TPL (b) on excitation wavelength observed in the low and high excitation intensity regimes.

SHG and TPL on excitation wavelength in the low and high excitation intensity regimes in Figs. 6(a) and (b), respectively.

In Fig. 6(a), it can be easily found that the slope for SHG does not change so much with excitation wavelength at low excitation intensities. It has a value around 1.50 except the smallest value of 0.83 at 765 nm, as indicated by the point A. At high excitation intensities, a rapid decrease in the slope of SHG is observed with increasing excitation wavelength. More interestingly, a negative slope for SHG is found for excitation wavelengths longer than 770 nm. In particular, a minimum slope of  $-1.54$  is found at 790 nm. To the best of our knowledge, this is the first experimental observation of negative slope for SHG. Previously, a saturation of SHG was reported and a negative slope for SHG was theoretically predicted [23]. In contrast to the nearly unchanged slope for SHG, the slope for TPL at low excitation intensities decreases with increasing excitation wavelength, as shown in Fig. 6(b). The slope for TPL is 2.17 at 750 nm while it is reduced to be 0.18 at 795 nm. In addition, the slope for TPL at high excitation intensities appears to be similar for all excitation wavelengths, ranging from 2.86 to 4.11.

### C. Physical Mechanism Responsible for the Competition Between SHG and TPL

Although both SHG and TPL scales with the square of the incident light intensity, there are two major differences between these two nonlinear optical processes. First, SHG is generally considered as a second-order process while TPL

is regarded as a third-order one because the former is proportional to the second-order susceptibility ( $\chi^{(2)}$ ) while the latter is proportional to the imaginary part of the third-order susceptibility ( $\text{Im}(\chi^{(3)})$ ). Second, TPL involves the generation of real carriers while SHG does not. As a result, TPL depends strongly on the absorption at the SH. In other words, it depends strongly on the density of states (DOS) at the energy level corresponding to the half of the excitation wavelength where real carriers are created through TPA. Therefore, it is thought that the DOS or the absorption at the half of the excitation wavelength, which determines the cross section of TPA, plays a crucial role in the competition between SHG and TPL. This is clearly reflected in the excitation wavelength dependent nonlinear optical response shown in Fig. 3. For short excitation wavelengths, the TPA occurs at the high-energy states of excitons which possess large DOS. Consequently, the nonlinear response spectrum is governed by TPL and SHG appears to be very weak. In comparison, the nonlinear response spectrum becomes dominated by SHG at long excitation wavelengths because the TPA occurs at the low-energy states of excitons with small DOS. For excitation wavelengths longer than 770 nm, the TPA can only occur at high excitation intensities through Rabi oscillation [32]. Therefore, there exists a wavelength dependent competition between SHG and TPL. The situation is similar when we consider the excitation intensity dependent competition between SHG and TPL at a fixed excitation wavelength. A dramatic change in SHG and TPL with increasing excitation intensity is expected to occur at 775 nm where a large change in DOS or TPA is expected with the reduction in the bandgap energy caused by the effects of bandgap renormalization and temperature rise. As schematically shown in Fig. 1, the reduction of the bandgap is equivalent to the excitation at higher-energy states which is benefit to TPL. As a result, we begin to observe the saturation of SHG or even a negative slope for it and the rapid increase of TPL.

Now let us try to understand the nonlinear optical response of ZnO NRs observed in the experiments based on the energy levels in ZnO NRs. For  $\lambda_{\text{ex}} = 750$  nm, we observe a slope of 2.17 for TPL and a slope of 1.22 for SHG at low excitation intensities, as shown in Fig. 3(a). It is thought that some SHG was reabsorbed and transferred to the TPL through single photon excitation. The smallest slope of 0.83 for SHG observed at 765 nm, which corresponds to the point A in Fig. 6(a), is thought to originate from the resonant excitation of the exciton ground state which is located at  $\sim 380$  nm. In this case, the strongest TPL was achieved at the lowest excitation intensity due to the resonant two-photon excitation of the exciton ground state and the resonant reabsorption of the SHG, as shown in Fig. 4(d).

With increasing excitation wavelength, the difference between the SHG and TPL intensities becomes larger at low excitation intensities and the nonlinear response spectrum becomes completely dominated by SHG. For excitation wavelengths shorter than 770 nm, one can see a cross point where the intensities of SHG and TPL are equal. It is noticed that the excitation intensity at the cross point becomes larger with increasing excitation wavelength. For excitation wavelengths

longer than 770 nm, we did not observe the cross point at the highest excitation intensity. In this case, the energy of two photons does not reach the ground state of excitons. Consequently, TPL is quite weak and SHG is dominant.

Basically, the excitons generated via TPA in the high-energy states of excitons will relax to the ground state of excitons through exciton-phonon scattering. This process will lead to an increase in the temperature of ZnO NRs. As a result, the bandgap energy of ZnO will be reduced with increasing temperature, resulting in the excitation of excitons in the states with higher energy or larger DOS. A positive feedback like this will lead to an avalanche process which facilitate the generation of TPL. We think this is the origin why a rapid increase in TPL or a large slope of more than 3.0 was observed at high excitation intensities. Actually, this suspicion is confirmed by the appearance of exciton emission for excitation wavelengths longer than 770 nm, as indicated by arrows in Fig. 3. At 775 nm, the exciton emission appeared at 375 nm. It was red shifted to  $\sim 390$  nm at 795 nm, indicating clearly the reduction in the bandgap energy due to the temperature rise in ZnO NRs.

A negative slope of  $-0.87$  for SHG was first observed at 775 nm in the high excitation intensity regime. If we consider the reduction in the bandgap energy and thus in the energy of exciton states, the appearance of negative slope can be attributed to the resonant excitation of the exciton ground state and the reabsorption of SHG through single photon excitation, which is similar to the phenomenon observed at 765 nm in the low excitation intensity regime. Accordingly, we obtained a largest slope for TPL which corresponds to the peak in Fig. 6(b) (point B'). It is noticed in Fig. 3 that the exciton emission begins to appear at 775 nm and it appears on the short wavelength side of the SHG peak. In this case, the energy of two photons was smaller than that of the exciton ground state. Previously, the excitation of exciton energy states by TPA was also observed in ZnO nanowires when the energy of two photons was smaller than that of the exciton ground state [32]. Rabi oscillation was proposed to explain the excitation of exciton energy states. We think that a similar process occurred in our case and the energy of the fs laser and SHG was transferred to the exciton energy states, leading to the rapid increase in TPL and the reduction of SHG. At 795 nm, the energy separation between the exciton emission and the excitation wavelength is large and the excitation of excitons through Rabi oscillation is suppressed. Consequently, the slope of SHG is recovered from  $-1.54$  at 790 nm to  $-0.05$  at 795 nm, as indicated by the point C in Fig. 6(a).

#### IV. CONCLUSION

We have systematically investigated the nonlinear optical properties of ZnO NRs by using a focused fs laser light with tunable excitation wavelength ranging from 750 to 795 nm. Both SHG and TPL were observed in the nonlinear response spectra measured at different excitation wavelengths. At high excitation intensities, it was found that the nonlinear response spectrum became dominated by TPL for excitation wavelengths shorter than 770 nm while it was still governed by

SHG for excitation wavelengths longer than 770 nm. For each wavelength, an excitation intensity dependent competition between SHG and TPL was observed and the nonlinear optical signals (SHG and TPL) exhibited different slopes in the low and high excitation intensity regimes. While a rapid decrease in the slope of SHG was found at high excitation intensities, a dramatic increase in the slope of TPL was observed. More interestingly, a negative slope for SHG was observed for excitation wavelengths longer than 770 nm. The reduction in the bandgap energy induced by the effects of bandgap renormalization and temperature rise, the resonant excitation of exciton ground state and the Rabi oscillation were proposed to interpret the competition between SHG and TPL and other nonlinear optical properties. The understanding of the nonlinear optical processes occurring in ZnO NRs and the competition between them will be helpful for controlling and engineering their nonlinear optical properties for various device applications.

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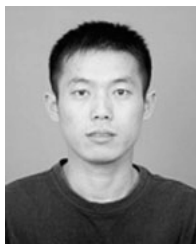




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