

Femtosecond laser ablation of ZnO nanorods for two-photon-pumped random lasing and optical data storage

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Received: 6 October 2011 / Published online: 26 November 2011
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Abstract Femtosecond laser ablation based on two-photon absorption was employed to cut ZnO nanorods into uniform ZnO nanoparticles of deep subwavelength size. The fabricated ZnO nanoparticles possess a shorter mean transport length for photons at the emission wavelength and a much smaller scattering cross section at the pump wavelength, leading to highly efficient two-photon-pumped random lasing with a low threshold of ~ 8 mJ/cm². It was demonstrated that the significant enhancement in two-photon luminescence after the irradiation of femtosecond laser pulses could also be utilized for realizing optical data storage.

1 Introduction

Random lasers made of randomly distributed scattering particles with appropriate gain have attracted great interest in

the last decade due to their potential application in realizing efficient light emitters [1–4]. In practice, one can employ either scattering particles with gain or scattering particles without gain that are immersed in a gain medium to realize random lasers. In the former case, ZnO nanostructures in various forms are utilized as the most popular scattering particles to achieve random lasing, including nanocrystallites [5], nanocomposites (e.g., ZnO@mesoporous silica) [6], nanorods [7], nanotubes [8], and nanoneedles [9], etc. So far, the physical mechanism for random lasing has been established based on different theoretical models and experimental observations [10–15]. Basically, random lasers can be classified into two types according to the feedback mechanism, i.e., random lasers with incoherent and coherent feedbacks. From the viewpoint of device application, however, it is highly desirable to fabricate efficient random lasers with low thresholds.

Physically, there are two ways to improve the performance of random lasers. One is to increase the scattering strength of nanoparticles which is characterized by the mean transport length of photons (l_t) in the media composed of randomly distributed nanoparticles. The other is to enhance the efficiency of the pump light which is also affected by the scattering and absorption of nanoparticles. In practice, random lasing can be easily realized by pumping the disordered medium with nanosecond or picosecond lasers. In contrast, there are few reports on the random lasing achieved by femtosecond (fs) laser pumping because of the very short pulse duration [5, 16]. In addition, it is quite difficult to realize random lasing with coherent feedback by using fs laser pumping. Although low-threshold two-photon-pumped ZnO nanowire lasers have been reported recently [17], how to realize two-photon-pumped random lasing (TP-PRL) with a low threshold remains to be a challenge. For ZnO nanoparticles whose emission wavelength appears at

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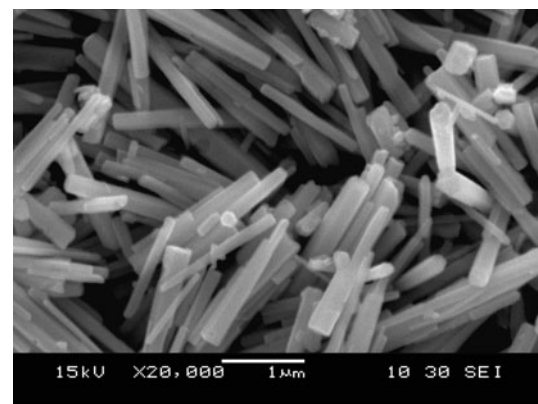
~ 390 nm, it has been suggested by theoretical analysis that random lasing with a lower threshold can be achieved by using two-photon pumping instead of single-photon pumping [18]. A detailed theoretical analysis reveals that the thresholds of both cases are independent of the absorption strength of the pump light [18]. Unfortunately, two-photon-pumped random lasers with thresholds lower than single-photon-pumped ones have not yet been realized.

In practice, most ZnO nanoparticles are synthesized by chemical methods and the accurate control of particle size during the fabrication process is a big challenge. In comparison, it is relatively easier to fabricate ZnO nanorods whose diameter can be accurately controlled to some extent. On the other hand, the interaction between fs laser pulses and various materials (including metals, semiconductors, and dielectrics) offers us the opportunity to create micro- and nanostructures on the surfaces of these materials whose feature size can be tailored [19]. It has been known that ripples with a subwavelength period can be induced on the surface of a material by fs laser pulses with an energy density just above the ablation threshold of the material [20, 21].

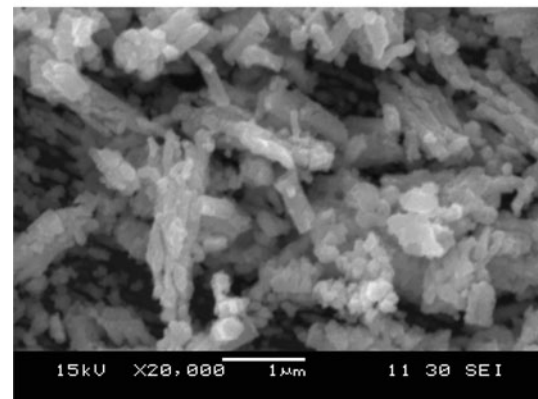
In this article, we report on fs laser ablation of ZnO nanorods and the highly efficient TPPRL from the resulting ZnO nanoparticles. It is found that ZnO nanorods can be chopped into identical pieces (nanodisks) by fs laser pulses whose energy density is above the ablation threshold. The feature size of ZnO nanoparticles can be controlled by adjusting the laser wavelength. The uniform ZnO nanoparticles obtained in this way function as an efficient random laser medium that renders more than two orders of magnitude enhancement in two-photon luminescence (TPL). TPPRL with a threshold as low as 8 mJ/cm^2 has been achieved by using fs laser pumping. We show that the significant enhancement in TPL after irradiation of fs laser pulses may find applications in efficient light emitters and optical data storage.

2 Experimental

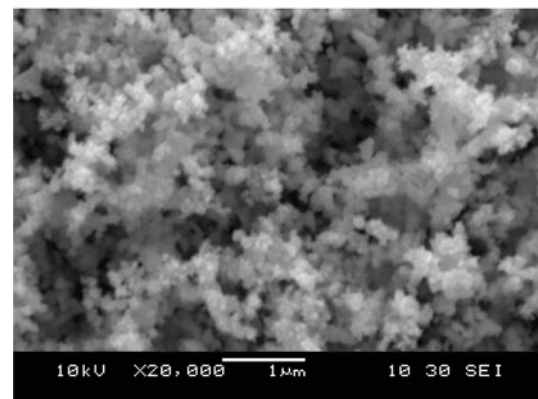
The ZnO nanorods used in our study were synthesized by using the method reported previously [22]. The synthesis process for ZnO nanorods can be described in three steps. First, 250-mL aqueous solutions of zinc acetate ($\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$) and triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$) 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 a lot of acidic and nonionic water and dried at 80°C for 24 hours



a



b



c

Fig. 1 SEM images of ZnO nanorods before (a) and after (b) and (c) fs laser irradiation (47 mJ/cm^2) of different times. (b) $t = 30$ s and (c) $t = 60$ s

to obtain ZnO nanorods. The SEM image of the synthesized ZnO nanorods is shown in Fig. 1(a). The average diameter and length of ZnO nanorods are measured to be ~ 250 nm and $\sim 2 \mu\text{m}$, respectively.

For the measurements of TPL, ZnO nanorods were densely packed into a $100\text{-}\mu\text{m}$ -thick sample cell made of two cover glass slides. The 720-nm laser light from an optical parametric amplifier (OperA Solo, Coherent) with a duration of 100 fs and a repetition rate of 1 kHz was focused

normally on the sample by using a lens with a focusing length of 150 mm. The sample cell was placed 20 mm away from the focus. The TPL from ZnO nanorods was detected at 45° with respect to the normal by using a fiber spectrometer with a resolution of 0.37 nm (USB2000+, Ocean Optics). The pump energy density was derived by accurately measuring the intensity distribution of the laser spot at the sample position by using a laser beam analyzer (HV1300UM, CDHC-Optoelectronics).

3 Results and discussion

3.1 Femtosecond laser ablation of ZnO nanorods

We irradiated an ensemble of ZnO nanorods with 720-nm fs laser pulses (~ 100 fs; 1 kHz) and observed for the first time the ablation of ZnO nanorods. Due to the large scattering cross section (SCS) of ZnO nanorods at 720 nm, the incident laser light will be randomly scattered by nanorods. In experiments, it is interesting to find that uniform nanodisks can be obtained provided that the irradiation time is sufficiently long. The SEM images for the samples containing ZnO nanorods irradiated by fs pulses (47 mJ/cm^2) for different times of 30 and 60 s are shown in Figs. 1(b) and 1(c). In Fig. 1(b), we can find the coexistence of the formed nanoparticles and few shorter nanorods. With a long irradiation time of 60 s, only nanoparticles with uniform size are left, as shown in Fig. 1(c).

A detailed investigation of the ablation of a single layer of ZnO nanorods by fs laser pulses revealed that most nanorods were chopped into nearly identical pieces with an average length of ~ 110 nm, as shown in Fig. 2. As a result, each nanorod is cut into ~ 20 shorter nanorods (or nanodisks) with a diameter of ~ 250 nm and a length of ~ 110 nm. In Fig. 2, the fs laser light is vertically polarized and nanorods were cut along horizontal direction. This situation is quite similar to that observed on the surfaces of various materials where ripples perpendicular to the polarization of laser

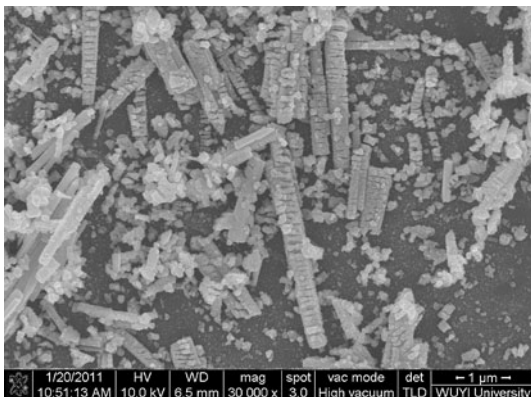


Fig. 2 SEM image showing the cutting of ZnO nanorods into identical nanodisks by fs laser pulses. The laser light is vertically polarized

light are formed [19–21]. In our case, the length of ZnO nanodisks appears to be much shorter than the laser wavelength. It has been reported that high-frequency laser-induced periodic surface structures (HFLIPSS) can be created on the surface of semiconductors that are transparent to the laser light [23], including ZnO. It is suggested that the second harmonic generation (SHG) by intense laser light plays an important role in the formation of such HFLIPSS [24]. The length of ZnO nanodisks obtained in our case is similar to the period of HFLIPSS formed on the surface of ZnO films. Therefore, we believe that the ablation of ZnO nanorods is quite similar to that of ZnO films. In experiments, we have investigated the relationship between the length of nanodisks and the laser wavelength. A linear dependence of the length of ZnO nanodisks on the laser wavelength is clearly observed, as shown in Fig. 3. It means that we can easily control the feature size of ZnO nanodisks by simply adjusting the laser wavelength. Since the diameter of ZnO nanorods is quite uniform, ZnO nanoparticles with controllable feature size and relatively uniform size distribution can be obtained by using fs laser ablation of ZnO nanorods.

3.2 Scattering cross section of ZnO nanorods and nanodisks

The SCS of ZnO nanorods (σ_{rod}) as a function of wavelength can be calculated by using the discrete dipole approximation (DDA) method [25]. In Fig. 4, we present the wavelength dependence of σ_{rod} for three typical cases in which the angles between the nanorod and the incident light are chosen to be $\theta = 90^\circ$, 45° , and 0° , respectively. In the calculation, the wavelength dependence of refractive index for ZnO is also considered [26]. It can be seen that σ_{rod} is large when the nanorod is perpendicular to the incident light ($\theta = 90^\circ$). In the case when the nanorod is parallel to the incident light ($\theta = 0^\circ$), σ_{rod} is small for wavelengths shorter than 700 nm and it increases rapidly after 700 nm. Thus, nanorods oriented randomly in space possess SCS in between these two

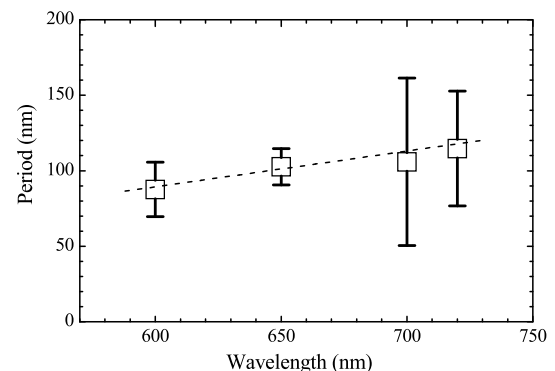


Fig. 3 Dependence of the length of ZnO nanodisks obtained by fs laser ablation on the laser wavelength

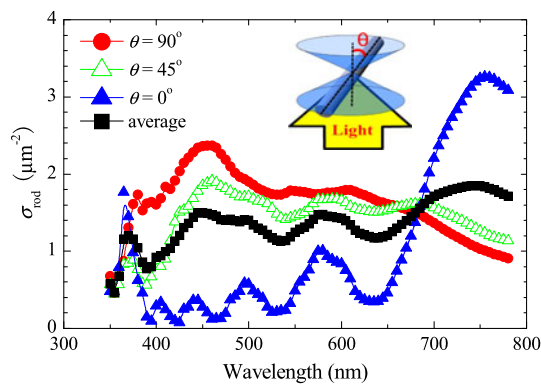


Fig. 4 Wavelength dependence of SCS for three typical cases in which the angles between the nanorod and the incident light are chosen to be $\theta = 90^\circ$, 45° , and 0° , respectively. The averaged value of SCS for these three typical cases is also presented

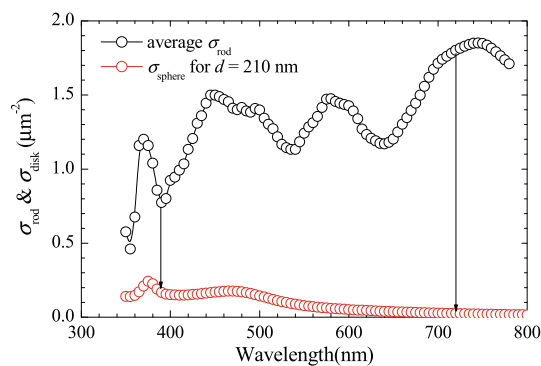


Fig. 5 Wavelength dependence of SCS for ZnO nanorods before (σ_{rod}) and after (σ_{disk}) fs laser irradiation. The two arrows indicate the changes of SCS at the emission and pump wavelengths

extreme cases. For simplicity, we use the average value of these three typical cases to approximate the averaged SCS of randomly oriented nanorods. At the emission wavelength of ZnO nanorods (~ 390 nm), the averaged value of σ_{rod} is estimated to be $\sim 0.78 \mu\text{m}^{-2}$.

To estimate the SCS of nanodisks (σ_{disk}) obtained by fs laser ablation, we will use nanospheres whose volume is equal to that of nanodisks to calculate their SCS. In our case, the diameter of the equivalent sphere is estimated to be ~ 210 nm. In Fig. 5, we present the wavelength dependence of σ_{rod} and σ_{disk} and compare their values at the emission (390 nm) and pump (720 nm) wavelengths. It is noticed that the SCS at 390 nm is reduced from 0.78 to $0.17 \mu\text{m}^{-2}$ when nanorods are changed into nanodisks. In addition, it is remarkable that the SCS at 720 nm decreases dramatically from 1.80 to $0.025 \mu\text{m}^{-2}$.

3.3 Two-photon-luminescence and two-photon-pumped random lasing

Physically, the threshold for TPPRL (I_{th}) is determined by both the mean transport length of photons in the disordered

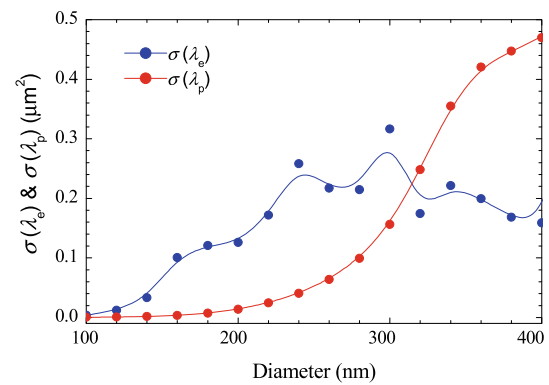


Fig. 6 Calculated SCS of ZnO nanospheres at the emission and pump wavelengths ($\sigma(\lambda_e)$ and $\sigma(\lambda_p)$) as a function of the diameter of nanospheres

medium at the emission and pump wavelengths ($l_t(\lambda_e)$ and $l_t(\lambda_p)$), i.e., $I_{\text{th}} \propto l_t(\lambda_e)l_t^{-1}(\lambda_p)$ [18]. The value of l_t is inversely proportional to the volume density (N) and SCS of scattering particles (σ), i.e., $l_t \propto 1/(N\sigma)$ [27]. When ZnO nanorods are cut into nanodisks by fs laser pulses, it is estimated that $l_t(\lambda_e)$ is reduced by a factor of ~ 4.3 because the significant increase in N (~ 20 times) and a slight decrease of $\sigma(\lambda_e)$ (~ 4.6 times). On the other hand, an increase of $l_t(\lambda_p)$ by a factor of 3.6 is expected at the pump wavelength because a dramatic reduction of $\sigma(\lambda_p)$. Consequently, one can anticipate a reduction of the threshold by more than one order of magnitude or a significant increase in TPL. In Fig. 6, we present the calculated $\sigma(\lambda_e)$ and $\sigma(\lambda_p)$ as a function of the diameter of nanospheres. In order to achieve TPPRL with a low threshold, one needs to get a large $\sigma(\lambda_e)$ but a small $\sigma(\lambda_p)$. Since $\sigma(\lambda_p)$ starts to decrease rapidly for nanospheres with a diameter of ~ 300 nm and the sharp reduction of $\sigma(\lambda_e)$ occurs at a smaller diameter of ~ 150 nm, it is easily understood that an appropriate diameter for nanospheres appears at around 220 nm.

A significant enhancement in TPL and efficient TPPRL are experimentally demonstrated by comparing the TPL of ZnO nanorods before and after the irradiation of fs laser pulses, as shown in Figs. 7 and 8. For pump energy densities smaller than 23.8 mJ/cm^2 , the TPL of ZnO nanorods increases quadratically with increasing pump energy density, exhibiting a signature of TPL [28–30], as manifested in Figs. 7(a) and 8(a). After that, a saturation and even a reduction of TPL occur with a further increase in pump energy density, indicating that the laser energy density reaches the ablation threshold of ZnO nanorods. At this time, we raised the laser energy density to 143 mJ/cm^2 and irradiated 10^4 pulses on ZnO nanorods. After that, we lowered the pump energy density and measured again the dependence of TPL on pump energy density. The results are presented in Figs. 7(b) and 8(a). It is noticed that a significant enhancement in TPL is achieved after the irradiation by 10^4 fs laser

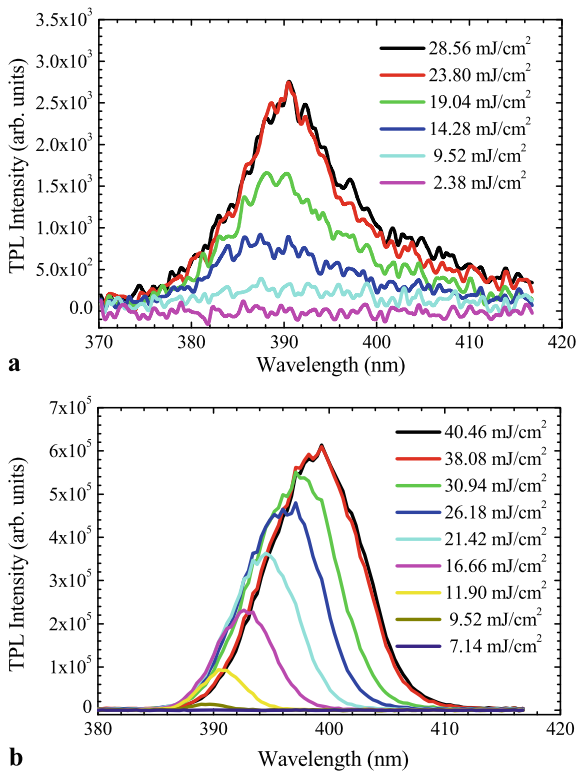


Fig. 7 TPL spectra of ZnO nanorods before (a) and after (b) irradiation by 10^4 fs laser pulses with an energy density of 143 mJ/cm^2

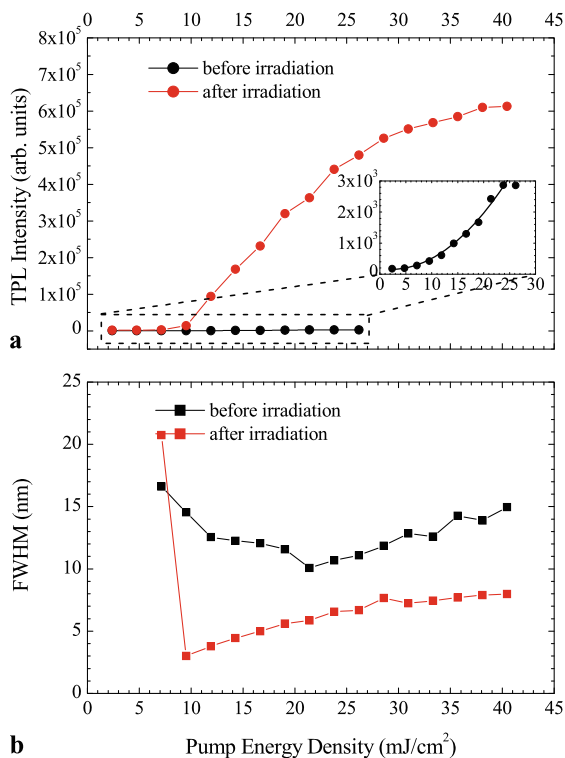


Fig. 8 Comparison of pump energy density dependence of TPL intensity (a) and FWHM (b) for ZnO nanorods before and after irradiation by 10^4 fs laser pulses with an energy density of 143 mJ/cm^2

pulses. More importantly, nonresonant random lasing [10] is clearly manifested in the sharp increase of TPL and the dramatic reduction of full width at half maximum (FWHM) at $\sim 8 \text{ mJ/cm}^2$, as shown in Figs. 8(a) and 8(b). An enhancement factor as large as ~ 200 is achieved at a pump energy density of 23.8 mJ/cm^2 . The evolution of the FWHM with increasing pump energy density for ZnO nanodisks is similar to those reported previously for two-photon-pumped ZnO nanoparticles with an average diameter of $\sim 5 \text{ nm}$ [5]. However, the threshold in our case is reduced by one order of magnitude as compared to the previous report which is $\sim 80 \text{ mJ/cm}^2$ [5], demonstrating an efficient TPPRL. We think that the reduction in threshold is achieved by deliberately choosing the size of ZnO nanoparticles for TPPRL, which has been interpreted in Fig. 6. In [5], the size of ZnO nanoparticles obtained by pulsed laser deposition is too small ($\sim 5 \text{ nm}$), leading to a weak scattering at the emission wavelength and a large threshold.

3.4 Optical data storage by using ZnO nanorods embedded in a PMMA film

The significant enhancement in TPL observed in ZnO nanorods after the irradiation of fs laser pulses may find applications in optical data storage. In order to demonstrate the use of ZnO nanorods in optical data storage, we have scanned the laser beam on the sample formed by densely packing ZnO nanorods. The energy density and scanning speed of the laser light were chosen to be 143 mJ/cm^2 and $38.2 \mu\text{m/s}$, respectively. Four straight lines were scanned on the sample. After that, we lowered the energy density of the laser to 38 mJ/cm^2 and measured the TPL along a straight line which is perpendicular to the four scanned lines. The result is shown in Fig. 9. A significant enhancement in TPL of more than 50 times is observed within the scanned lines, implying that optical information can be recorded (or written) into ZnO nanorods by irradiating fs laser pulses with a

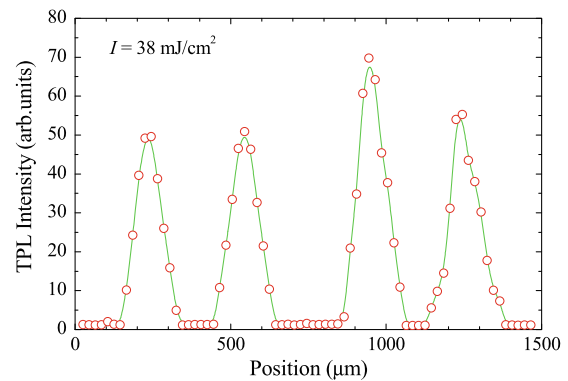


Fig. 9 TPL intensity measured at an energy density of 38 mJ/cm^2 along a straight line which is perpendicular to the four scanned lines irradiated by fs laser pulses with an energy density 143 mJ/cm^2 and a scanning speed of $38.2 \mu\text{m/s}$

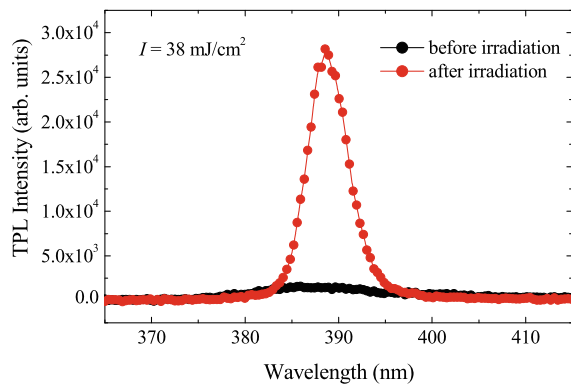


Fig. 10 TPL intensity of ZnO nanorods randomly distributed in a PMMA film measured at an energy density of 38 mJ/cm^2 before and after irradiation by 10^4 fs laser pulses with an energy density of 285.6 mJ/cm^2

high energy density. Since both the writing and reading processes rely on two-photon absorption which is proportional to the square of the laser intensity, the pixel for optical data storage can be dramatically reduced by decreasing the laser spot.

We have also fabricated PMMA films in which ZnO nanorods were uniformly distributed by spinning coating. In this case, the scattering strength of ZnO nanostructures is reduced to some extent due to the increase in the background refractive index. However, an enhancement factor as large as ~ 16 can still be obtained at an energy density of 38 mJ/cm^2 after irradiation of 10^4 fs laser pulses with an energy density of 285.6 mJ/cm^2 , as shown in Fig. 10. This contrast is large enough for optical data storage. Considering the capacity and speed of optical data writing and reading, more experimental investigations are needed in order to explore the application of ZnO nanorods in optical data storage.

4 Conclusion

In summary, we have investigated for the first time the ablation of ZnO nanorods by fs laser pulses and demonstrated its application in TPPRL and optical data storage. It is revealed that ZnO nanorods can be chopped into ZnO nanodisks with uniform size which can be varied by adjusting laser wavelength. A significant enhancement of more than two orders of magnitude in TPL as well as a low threshold of 8 mJ/cm^2 for TPPRL has been achieved by using the fabricated ZnO nanodisks. The application of fs laser ablation of ZnO nanorods in the fabrication of optical data storage media is also explored.

Acknowledgements The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant Nos. 10974060, 51171066, and 1111120068) and the project for high-level professionals in the universities of Guangdong Province, China.

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