Enhanced upconversion luminescence from ZnO/Zn hybrid nanostructures induced on a Zn foil by femtosecond laser ablation

Hui Li,1 Cheng-Yun Zhang,2 Xian-Feng Li,1 Jin Xiang,1 Shao-Long Tie,3 and Sheng Lan1,*

1Guangdong Provincial Key Laboratory of Nanophotonic Functional Materials and Devices, School of Information and Optoelectronic Science and Engineering, South China Normal University, Guangzhou, China
2School of Physics and Electronic Engineering, Guangzhou University, Guangzhou 510640, China
3School of Chemistry and Environment, South China Normal University, Guangzhou, China
*slan@scnu.edu.cn

Abstract: ZnO/Zn hybrid nanostructures including nanowires and nanonets were induced on a Zn foil by using 400-nm femtosecond (fs) laser pulses with a low repetition rate of 1 kHz and duration of 100 fs. The laser fluence was chosen to be slightly above the ablation threshold of Zn. The luminescence of the formed ZnO/Zn hybrid nanostructures was examined by using fs laser pulses with a high repetition rate of 76 MHz and duration of ~130 fs through both single-photon and multiphoton excitation. While the luminescence spectrum under the single-photon excitation exhibited a single peak at ~480 nm, a broadband upconversion luminescence with many ripples was observed under the multiphoton excitation. More interestingly, the upconversion luminescence of the ZnO/Zn hybrid nanostructures was significantly enhanced by the underlying Zn nanostructures which induced strongly localized electric field. The enhancement of the upconversion luminescence was verified by the short lifetime of only ~79 ps observed for the ZnO/Zn hybrid nanostructures, which is nearly one order of magnitude smaller as compared with the luminescence lifetime of the ZnO nanorods synthesized by using the chemical coprecipitation method. The localization of electric field in the ZnO/Zn hybrid nanostructures was confirmed by the numerical simulations based the finite-difference time-domain technique.

OCIS codes: (140.3390) Laser materials processing; (190.4180) Multiphoton processes; (190.7220) Upconversion; (160.6000) Semiconductor materials.

References and links
1. Introduction

As a semiconductor with wide bandgap (E_g~3.37 eV) and large exciton binding energy (~60 meV), ZnO has attracted great interest in the last two decades due to its potential applications in the fabrication of various functional devices [1–6]. With the rapid development of nanometer science and technology, ZnO nanomaterials and nanostructures in different fashions have been successfully synthesized by various chemical methods [7–12]. In comparison, very few ZnO nanomaterials or nanostructures are fabricated by physical methods and femtosecond (fs) laser ablation appears to be one of the most useful physical methods. For instance, Zeng et al. reported the fabrication of ZnO nanoparticles in a non-equilibrium environment (e.g., laser ablation-induced extreme conditions) and zinc-rich annealing [13]. It has been known for a long time that periodic surface structures such as ripples can be induced on the surfaces of different materials, including dielectrics, semiconductors and metals [14–19], by using high-power lasers. It was suggested that such laser-induced periodic surface structures (LIPSS) originated from either the interference between the surface scattered wave induced by surface roughness and the incident wave [20,21] or the interference between the surface plasmon polaritons (SPPs) induced by fs laser irradiation with the incident wave [22–28]. For some metals that are easily oxidized in air (e.g., Al, Ti, and Zn etc.), oxidation usually occurs in the ablation process because of the high-temperature induced by the fs laser pulses [29,30]. As a result, a thin layer of oxide, which is generally a semiconductor, is created on the metal surface. The formation of such thin oxide layer may significantly alter the interaction of the metal with the fs laser pulses and affect the subsequently ablation process. Recently, we have demonstrated the formation of LIPSS with deep subwavelength periods as small as about one-tenth of the irradiating fs laser light wavelength created on the surface of a Ti foil by exploiting laser-induced oxidation and third harmonic generation [30]. In this case, TiO_2 nanowires with a feature width of ~50 nm were created on the surface of a Ti foil. Apparently, the TiO_2/Ti hybrid nanostructures are attractive for the fabrication of functional devices if one can exploit the electric field enhancement originating from the SPPs. Unfortunately, TiO_2 is not a semiconductor with good emission properties. Previously, a nanometer-scaled plasmonic laser has been demonstrated by utilizing the hybrid plasmonic waveguide with optical modes a hundred times smaller than the diffraction limit [31]. It was composed of a CdS nanowire placed on a thin Ag film. Therefore, one can fully exploit both the emission properties of the semiconductor and the plasmonic properties of the metal by deliberately selecting the metal for creating semiconductor/metal hybrid nanostructures. In this way, plasmonic lasers with a configuration similar to that reported previously may be realized by one-step fabrication.

Zn is a metal which has been widely applied in industry. It is easily oxidized in air if the temperature is sufficiently high, creating a thin ZnO layer. The formation of the thin ZnO layer will modify the interaction of the Zn with fs laser pulses, leading to the formation of ZnO/Zn nanostructures. The ‘fusion’ of ZnO and Zn in the ablation process will greatly alter the linear and nonlinear optical properties of ZnO. Since ZnO has a high melting point, it makes it possible to investigate the nonlinear optical properties of the ZnO/Zn hybrid nanostructures under high excitation densities and compared them with those of the ZnO nanorods (NRs) synthesized by using chemical methods.

In this article, we report on the formation and characterization of ZnO/Zn hybrid nanostructures including nanowires and nanonets. It was found that nanowires and nanonets with a feature size as small as ~50 nm were obtained upon the ablation of the surface of a Zn foil. The formed ZnO/Zn hybrid nanostructures could emit strong upconversion luminescence under the excitation of fs laser pulses with high repetition rate. The enhanced radiative
recombination rate induced by the strongly localized electric field in the nanostuctures was confirmed by the measured short lifetime of only 79 ps. The hybrid nanostructures reported in this work, especially the nanowires, are promising candidates for the fabrication of nanometer-scale plasmonic lasers.

2. Sample preparation and experimental setup

In our experiments, ZnO/Zn hybrid nanostructures were fabricated on a 0.5-mm-thick Zn foil by irradiating fs laser pulses at a wavelength ($\lambda_{ab}$) of 400 nm which was obtained by doubling the frequency of a fs laser amplifier (Legend, Coherent) with a BBO crystal. The duration and repetition rate of the laser pulses were ~100 fs and 1 kHz, respectively. The Zn foils, which are polycrystalline materials with a purity of 99%, were purchased from MTI Corporation, China. The laser beam with a diameter of ~5.0 mm and a Gaussian profile was focused normally on the surface of the Zn foil by using a lens with a focusing length of $f = 150$ mm, producing an excitation spot of ~40 $\mu$m in diameter (full width at $1/e^2$ of the laser intensity). The laser fluence (F), which is defined as the energy of a single pulse divided by the area of the excitation spot, was adjusted by using the combination of a waveplate and a polarizer. The ablation was carried out in air by irradiating the surface of the Zn foil with different pulse numbers (N). The morphology of the formed nanostructures was examined by scanning electron microscopy (SEM) (Ultra55, Zeiss) and their compositions were analyzed by using energy dispersive spectroscopy (EDS). The ZnO NRs used for comparison were synthesized by using the chemical method reported previously [32].

For the characterization of nonlinear optical properties, the fs laser light from a Ti:sapphire oscillator (Mira 900S, Coherent) with a pulse duration of ~130 fs and a repetition rate of 76 MHz was focused on the sample by using the objective lens (60 × , NA = 0.85) of an inverted microscope (Axio Observer A1, Zeiss). The optical signals were collected by using the same objective lens and directed to a spectrometer equipped with a charge-coupled device for spectrum analysis. The luminescence lifetime of the ZnO/Zn hybrid nanostructures and ZnO NRs was measured by using a spectrometer based on the time correlation of single photon counting (LifeSpec-1400, Edinburgh Instruments).

3. Results and discussion

3.1 Morphology of ZnO/Zn hybrid nanostructures induced on the surface of a Zn foil

In order to obtain ZnO/Zn hybrid nanostructures, we first employed the 400-nm fs laser light to ablate the surface of the Zn foil. In our experiments, we adjusted either the laser fluence or the pulse number. The surface morphology of the Zn foil after the ablation was examined by SEM observations. Some typical results are shown in Fig. 1 where ZnO/Zn nanowires and nanonets are observed. In Fig. 1(a), we show some long and straight ZnO/Zn nanowires with a feature width as narrow as ~50 nm. A magnified image is shown in Fig. 1(b). Different from the LIPSS reported previously, the width of the ZnO/Zn nanowires was much smaller than the period which was more than 250 nm. With increasing irradiation pulse number, we observed the formation of ZnO/Zn nanonets rather than nanowires, as shown in Figs. 1(c). In this case, short and curvy ZnO/Zn nanowires were connected with each other to form a net structure with some nanoparticles appearing at the junctions. Such nanostructures are quite different from the LIPSS reported previously [14–19]. In addition, they are also distinct from the nanostructures induced by the 800-nm fs laser light, as shown in Fig. 1(d). In order to confirm the formation of ZnO, we performed EDS measurements for the fabricated nanostructures. A typical result is shown in Fig. 1(e) where the element of oxygen (O) was detected. In comparison, no oxygen was found in the EDS spectrum of the un-ablated area of the Zn foil, indicating clearly the formation of ZnO during the ablation process.
3.2 Luminescence of the ZnO/Zn hybrid nanostructures under single photon excitation

The luminescence of the ZnO/Zn hybrid nanostructures generated by single photon excitation was characterized by using the 380-nm fs laser light with a high repetition rate of 76 MHz. The evolution of the luminescence spectrum with increasing excitation intensity is shown in Fig. 2(a) where a broad luminescence band peaking at ~480 nm is observed. The defects introduced in the ablation process such as oxygen vacancies (V$_{O}$), zinc interstitials (Zn$_{i}$) and surface defects are responsible for the observed luminescence. It has been reported that Zn$_{i}$ can be introduced in ZnO nanoparticles fabricated by fs laser ablation [13]. While V$_{O}$ in ZnO emits green light at ~530 nm, Zn$_{i}$ and surface defects emit blue light in the wavelength range of 420–480 nm [13,34–36]. Since the luminescence peak appeared at ~480 nm, it was thought that the luminescence under single photon excitation was dominated by the emission from Zn$_{i}$ and surface defects. In Fig. 2(b), we present the dependence of the luminescence intensity on the excitation intensity plotted in a double logarithmic coordinate. The slope extracted by fitting the experimental data is about ~0.76.
3.3 Nonlinear optical responses of the ZnO/Zn hybrid nanostructures under multiphoton excitation

The nonlinear optical responses of the formed ZnO/Zn hybrid nanostructures were examined by using fs laser pulses with a high repetition rate of 76 MHz at different excitation wavelengths ($\lambda_{\text{ex}}$) ranging from 750–800 nm, as shown in Fig. 3. No obvious difference was found between the luminescence spectrum of the ZnO/Zn nanowires and that of the ZnO/Zn nanonets. In each case, the dependence of the luminescence spectrum on the excitation intensity was also measured.

First, let’s see the difference observed in the luminescence spectrum when the excitation wavelength was varied. For $\lambda_{\text{ex}} = 750$ nm, only upconversion luminescence was observed in the nonlinear response spectrum. However, the second harmonic generation (SHG) began to appear at 390 nm when $\lambda_{\text{ex}} = 780$ nm was used. The SHG intensity became stronger for $\lambda_{\text{ex}} = 800$ nm. In addition, the upconversion luminescence on the short-wavelength side of the second harmonic (SH) became visible, implying that a three-photon process was involved in the generation of the upconversion luminescence.

Then, let’s examine the evolution of the luminescence spectrum with increasing excitation intensity under different excitation wavelengths. In all cases, the luminescence spectrum appeared to be smooth with a peak at ~530 nm at low excitation intensities. This emission originated mainly from the defect levels of oxygen vacancies (V$_{O}$). For $\lambda_{\text{ex}} = 750$ nm, the luminescence became gradually dominated by the emission at ~400 nm, which is attributed to the emission from free excitons, with increasing excitation intensity, as shown in Fig. 3(a). In comparison, a nearly flat luminescence band was observed for $\lambda_{\text{ex}} = 780$ nm at high excitation intensities. When $\lambda_{\text{ex}} = 800$ nm, the luminescence peak was remained at ~530 nm as the excitation intensity was increased. In all cases, many small peaks began to appear on the luminescence band at high excitation intensities, implying the selective enhancement in the luminescence at some wavelengths. They were thought to originate from the formation of wavelength dependent “hot spots” in the ZnO/Zn hybrid nanostructures.

Finally, let’s see the dependence of the luminescence intensity on the excitation intensity which is plotted in a double logarithmic coordinate for the three excitation wavelengths, as shown in Figs. 3(b), 3(d) and 3(f). By fitting the experimental data, a slope between 2.0 and 3.0 was found in the low excitation intensity regime. In the high excitation intensity regime, a slope between 1.0 and 1.6 was obtained due to the saturation of the upconversion luminescence. For $\lambda_{\text{ex}} = 750$ nm, a slope of ~2.16 was extracted, implying that the upconversion was dominated by a two-photon process. In contrast, a slope of ~3.25 was derived for $\lambda_{\text{ex}} = 800$ nm, indicating that the upconversion became dominated by a three-
photon process. The situation for $\lambda_{ex} = 780$ nm was in between these two cases and a slope of $\sim 2.5$ was observed.

Fig. 3. Luminescence spectra of the ZnO/Zn hybrid nanostructures under the excitation of 750-nm (a), 780-nm (c) and 800-nm (e) fs laser pulses with different laser fluence. The dependence of the luminescence intensity on the laser fluence and the fitting of the experimental data for the three cases are presented in (b), (d) and (f), respectively.

As compared with the ZnO/Zn hybrid nanostructures, the upconversion luminescence of the ZnO NRs was not effective under the same excitation condition. It means that the electric field enhancement provided by SPPs plays a crucial in the generation of highly efficient upconversion luminescence. In Fig. 4, we show the microscope images of the upconversion luminescence observed at $\lambda_{ex} = 750$ nm for different excitation intensities. Extremely strong luminescence was observed at $F = 50.40$ mJ/cm$^2$, as shown in Fig. 4(c).
3.4 Lifetime of the upconversion luminescence of the ZnO/Zn hybrid nanostructures

It has been shown that the upconversion luminescence of the ZnO/Zn hybrid nanostructures was enhanced significantly as compared with that of the ZnO NRs. However, the enhancement in radiative recombination rate needs to be verified by measuring the lifetime of the upconversion luminescence. In Fig. 5, we compared the luminescence lifetime measured for the ZnO/Zn hybrid nanostructures and ZnO NRs. Since two decay processes were found in the decay of the luminescence, we employed biexponential fitting to derive the decay times for the two processes. For the ZnO NRs, the time constant for the fast decay is extracted to be $\tau_1 \sim 590$ ps. In sharp contrast, the time constant for the fast decay obtained for the ZnO/Zn hybrid nanostructures was only $\tau_1 \sim 79$ ps. It means that the radiative recombination rate has been increased by nearly one order of magnitude in the ZnO/Zn hybrid nanostructures.

3.5 Strongly localized electric field induced by ZnO/Zn hybrid nanostructures

Previously, it has been shown that the formation of a thin TiO$_2$ layer on the surface of a Ti foil can strongly localize the electric field of the incident light in the TiO$_2$ layer, leading to the ablation of the TiO$_2$ layer [30]. Similarly, it is expected that strongly localized electric field can also be induced in ZnO/Zn hybrid nanostructures. In our case, the intensity of the upconversion luminescence is determined by the electric field enhancement factor at both the excitation wavelength (750–800 nm) and the emission wavelength (400–600 nm). For the two-photon-induced luminescence, the intensity of the upconversion luminescence ($I_{\text{up}}$) can be expressed as follows [33]

$$I_{\text{up}} = \mu f_1^2(\lambda_{\text{ex}}) f_2^2(\lambda_{\text{em}}) I_{\text{in}},$$  \hspace{1cm} (1)

where $f_1(\lambda_{\text{ex}}) = |E(\lambda_{\text{ex}})/E_0|$ and $f_2(\lambda_{\text{em}}) = |E(\lambda_{\text{em}})/E_0|$ represent the electric field enhancement factor at the excitation and emission wavelengths and $I_{\text{in}}$ is the intensity of the incident light. For simplicity, we simulated by using the finite-difference time-domain (FDTD) technique the distribution of electric field intensity in ZnO/Zn nanowires, whose structure is schematically shown in Figs. 6(a) and 6(c), at $\lambda_{\text{ex}} = 800$ nm and $\lambda_{\text{em}} = 500$ nm. Here, the length of the ZnO/Zn nanowires was assumed to be infinite while they width and height were chosen to be 50 and 10 nm. The complex refractive indices for ZnO [37] and Zn [38] were chosen to be 2.04 + 0.42i and 1.995 + 1.50i at 500 nm and 1.96 + 0.399i and 1.87 + 2.51i at 800 nm, respectively. We employed non-uniform grid sizes and perfectly matched layer boundary condition in the numerical simulations. As shown in Figs. 6(b) and 6(d), one can see
an enhancement of electric field intensity by a factor of 3–5 in the ZnO/Zn nanowires as compared with that on the surface of Zn for both excitation polarizations, which is responsible for the significantly enhanced upconversion luminescence observed in the experiments. When the polarization of the incident light was perpendicular to the nanowires, a further enhancement of electric field intensity was observed at the two edges of each nanowire, similar to the evanescent electric field appearing in nanofibers.

Fig. 6. Schematics showing the excitation of the ZnO/Zn hybrid nanowires by using fs laser light with polarization perpendicular (a) and parallel (c) to the ZnO/Zn nanowires. (b) and (d) present the simulated electric field intensity distributions for the excitation schemes shown in (a) and (c), respectively.

4. Conclusion

In summary, we report on the significantly enhanced upconversion luminescence from the ZnO/Zn hybrid nanostructures created on the surface of a Zn foil by using fs laser ablation. It was confirmed that the luminescence lifetime of the ZnO/Zn hybrid nanostructures was reduced by nearly one order of magnitude as compared with the ZnO NRs synthesized by using the chemical coprecipitation method. It was revealed by FDTD simulation that the strongly localized electric field induced by the ZnO/Zn hybrid nanostructures was responsible for the enhancement of the upconversion luminescence. Our findings are helpful for the design and fabrication of ZnO/Zn hybrid nanostructures for practical applications such as nanometer-scaled plasmonic lasers.

Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (NSFC) (Grant Nos. 51171066 and 11374109).