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Super-radiance of excitons in a single ZnO tetrapod nanostructure has been observed. The emitted pulses exhibited very short duration, and the emission peak intensity exhibited exponential increase with the increased pump density. Multiple narrow emission peaks with short peak spacing have been observed in the emission spectra of a single ZnO tetrapod nanostructure. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3000612]

Excitons are bound electron-hole pairs,[1,2] which can play essential role in light emission diodes,[3,4] or in photovoltaic and sensing applications.[5,6] Excitons are Bose quasiparticles in bulk, while at low temperatures, Bose–Einstein condensates of excitons could occur.[7–9] With the rapid development of nanotechnology, many excitonic phenomena have been observed, such as Fermic state filling of excitons observed in quantum dots.[10–14] Thus, study of the coherent emission from a single nanostructure is needed to improve our understanding of excitonic processes in nanomaterials.

Lasing and cooperative emissions (super-radiance and superfluorescence) form a family of coherent emissions. Super-radiance was predicted in 1954,[15] but the first observation was reported in 1973.[16] More recently (in 1995), the super-radiance of Frenkel excitons in the quasi-quantum-wire structure was reported.[17] Super-radiance is the emission of a macroscopic dipole, which is formed by excitons in a correlated state. In superfluorescence, which is a similar cooperative emission, there is no initial macroscopic dipole and thus there is a delay between the superfluorescence emission peak and the excitation pulse.[18] Furthermore, the radiative decay rate of cooperative emissions is proportional to the number of excitons; and the density of excitons in a correlated state is higher than that of an uncorrelated state.

Many factors influence the correlation of excitons, such as excitonic density, duration of excitation laser pulse, and size confinement effect in mesoscopic systems. We discuss them as follows:

For the lowest-energy state, the radiative decay rate is[19]

$$2\gamma = 64\pi\left[\frac{R}{a_B}\right]^3 \gamma_s. \tag{1}$$

For high excitonic states (n), the radiative decay rate is decreased to

$$2\gamma_n = \frac{2\gamma}{n^2} = \frac{1}{n^2}64\pi\left[\frac{R}{a_B}\right]^3 \gamma_s, \tag{2}$$

here $\boldsymbol{R}$ is the radius of nanocrystal, n is the principal quantum number for the center of mass motion, and $\gamma_s \equiv 4|\mu_{cv}|^2/3\hbar\lambda^3$ is the spontaneous emission rate of band-to-band transitions. For nanocrystal, the factor $64\pi[\boldsymbol{R}/a_B]^3$ is very large ($\sim 10^7$). Our calculation results show that super-radiance decay times are 39 and 156 fs for the two lowest states, same order as the excitation pulse duration. In this calculation, we take $\boldsymbol{R}=120$ nm, $\lambda=385$ nm, $\varepsilon=8.34$,[20] $\hbar\Delta_{\mathrm{LT}}=4|\mu_{cv}|^2/\varepsilon a_B^3=1$ meV.[19] Therefore, at high-density ultrashort pulsed laser excitation, the heat phonon does not have enough time to destroy the correlation of excitons before the completion of super-radiance. In other words, exciton super-radiance with short decay time is readily achievable in nanomaterials under ultrashort-pulsed laser excitation.

Pump density-emission peak intensity relationship is the most important criterion for distinguishing super-radiance and lasing. For lasing, two linear lines (one stands for fluorescence and another for lasing) with different slopes appear in this relationship. For super-radiance, the emission peak intensity ($\boldsymbol{I}_e$) is exponentially proportional to the pump density ($\boldsymbol{I}_p$). For bulk material, $\boldsymbol{I}_e$ is almost proportional to the square of $\boldsymbol{I}_p$; i.e., $\boldsymbol{I}_e \propto \boldsymbol{I}_p^{2-\beta}$, where $\beta<0.5$, which exact value is dependent on $\boldsymbol{I}_p$.[15–17]

To identify the characteristics above, we designed an experiment as follows: A femtosecond ultraviolet laser with wavelength around 355 nm and pulse duration of 100 fs was used as a pump source. A spectrometer (C5094) connected to a streak camera (FESCA C6860) was used as a detector. To ensure that only one single nanostructure was detected, we used a lens system to collect the emission and form an amplified (about two to three times) image of emitting sample on the input slits of the spectroscope. The input slit of the spectroscope is a vertical slit; while the input slit of streak camera is a horizontal one. We adjusted slit width for both slits to 10 μm. Furthermore, the diameter of the laser focal spot on the sample was 12 μm. The separation among crystallites in our sample was larger than 10 μm in order to obtain the emission signals from a single nanostructure.

The sample was zinc oxide tetrapod nanostructure. ZnO tetrapods were synthesized according to previously published procedure.[21] Scanning electron microscope (SEM) image and its cathodoluminescence image are shown in Figs. 1(a) and 1(b), respectively. Figures 1(b) and 2(b) are recorded by a field emission scanning electron microanalyzer (model: Siron 200, FEI) connected to a cathodoluminescence system (model: MonoCL, Gatan, UK).

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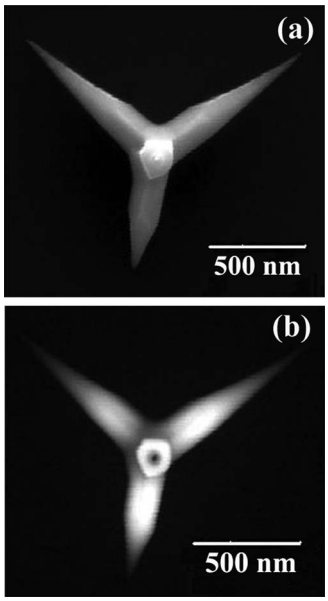

FIG. 1. (a) SEM image of ZnO tetrapod; (b) the cathodoluminescence image of the zinc oxide tetrapod.

The fluorescent spectrum of the ZnO tetrapod crystals excited by ultraviolet light (355 nm) at room temperature is shown in Fig. 2(a); and the corresponding cathodoluminescence spectrum is shown in Fig. 2(b). The bandwidth in Fig. 2(b) is slightly larger than that in Fig. 2(a) because the temperature of the sample will rise at cathode ray excitation in vacuum.

At low-density excitation, the fluorescent decay time is 443 ps, as shown in Fig. 3(a). At high-density excitation, pulse duration of 1.9 ps (equal to the resolution of the measurement system) without delay is detected, as shown in Fig. 3(b). This short pulse duration without delay demonstrates that it does not come from superfluorescence.

The relationship between pump density and emission output peak intensity is shown in Fig. 4. When the excitation peak density is lower than 1 mJ/cm^2, fluorescence with a linear pump-emission relationship (dashed line in Fig. 4) and fluorescent decay time of 443 ps is shown. When the excitation peak density is higher than 1 mJ/cm^2, the emission is a

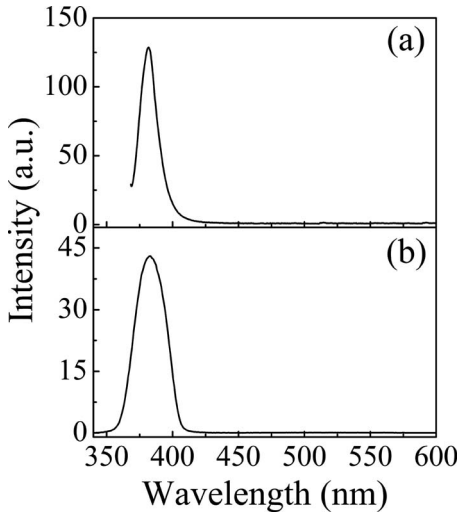

FIG. 2. The room temperature emission spectra of ZnO tetrapod: (a) photoluminescence, excited by ultraviolet light and (b) cathodoluminescence.

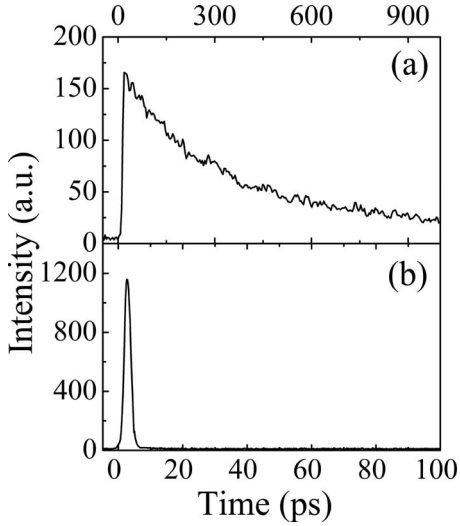

FIG. 3. The transient behaviors of a single ZnO tetrapod: (a) low-density excitation (full scale is 1000 ps); (b) high-density excitation (full scale is 100 ps).

short pulse, and the pump-emission relationship becomes an exponential line: $I_e \propto I_p^{2.43}$ (solid line in Fig. 4). Here the exponential factor is larger than 2, and the reasons for this observation require further study. The exponential intensity dependence and short emission duration without delay indicate that super-radiance occurs in a single ZnO tetrapod nanostructure.

Our experimental results show that the spectra of super-radiance have quantized subpeaks with peak separations of 6.3, 5.5, and 4.8 meV, as shown in Fig. 5. We calculate the exciton-exciton scattering band (P band) based on[22]

$$P_n = E_{\mathrm{ex}} - E_b^{\mathrm{ex}}\left(1 - \frac{1}{n^2}\right) - \frac{3}{2}kT, \tag{3}$$

which results in peak separations of $P_2 - P_3 = 8.3$ meV, $P_3 - P_4 = 2.9$ meV, $P_4 - P_5 = 1.4$ meV, and $P_5 - P_6 = 0.7$ meV. The calculated results above demonstrate that the emission spectrum of super-radiance differs from P band (P band also reflects the excitonic states). Furthermore, the linewidths and separations of these quantized spectra are much narrower than the linewidth and mode separations of short laser cavity, which depends on the length and the reflectivity of the cavity.[23] Therefore, Fig. 5 shows an unknown phenomenon. We propose a possible explanation of this experimental observation as follows: For different exciton densities (this can result from different densities of pump laser, different times during a laser pulse, and different arms of the tetrapod crys-

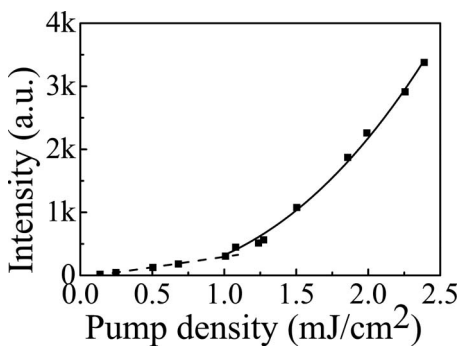

FIG. 4. The relationship between emission peak intensity and pump density.

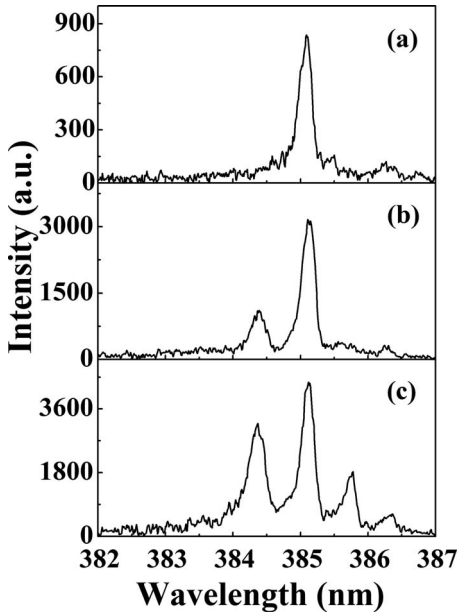

FIG. 5. Super-radiance spectra from a single ZnO tetrapod nanostructure (at the peak pump density of 1.1–1.2 mJ/cm^2).

tal), different mesoscopic dipoles appear, and result emissions with different quantized subpeaks. At femtosecond excitation condition, it is possible that one mesoscopic dipole forms in one arm after one pulse excitation. If all quantized mesoscopic dipoles of the four arms in all detected pulses are the same, the emission will only have one single peak as shown in Fig. 5(a). If four quantized mesoscopic dipoles appear, one in each tetrapod arm, the emission will have four subpeaks as shown in Fig. 5(c).

It should be noted that while super-radiance phenomena can be observed in a single nanostructure, the features of a super-radiance emission would be averaged out in an ensemble of nanostructures. As the excitation density increases above the super-radiance threshold of a single nanostructure, more nanostructures will exhibit super-radiance emission. The number of nanostructures contributing to super-radiance emission is expected to increase linearly with the increase in the pump density. Thus, the observed emission peak intensity will be linearly proportional to the pump density. In addition, in an ensemble of nanostructures there is usually a size distribution, resulting in different emission wavelengths of nanostructures with different sizes, resulting in broadening of the observed emission and possible masking of the peak splitting observed in super-radiance emission. Both of these factors will result in masking of the characteristic features of super-radiance, which would cause mistaken identification of super-radiance as lasing.

To summarize, emission from single ZnO tetrapod nanostructures under ultrashort-pulsed excitation was studied. Under high excitation density, super-radiance emission was observed, characterized by a very short emission duration and absence of a delay time. Multiple peaks were observed from a single nanostructure, and the peak separation was different from the expected values for separation of peaks due to exciton-exciton scattering and mode spacings in a short ZnO cavity.

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