Ultrasensitive femtosecond time-resolved fluorescence spectroscopy for relaxation processes by using parametric amplification

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We report the gain factor, detection limit, and linearity of a femtosecond time-resolved spectrometer for ultraweak fluorescence based on a 400 nm pumped femtosecond noncollinear optical parametric amplifier. By employing the parametric fluorescence amplifier, the time-resolved fluorescence spectra of Rhodamine 6G dye in ethanol was measured. It is proved that a good spectral fidelity has been achieved in the measurement of fluorescence spectra with this technique. The measured gain factor of this parametric fluorescence amplifier is found to be $\sim 1.2 \times 10^6$, and the detection limit is 5.1 aJ per pulse, corresponding to 15 fluorescence photons at 580 nm. With this technique, we have acquired the transient fluorescence spectra as well as the fluorescence decay profile of CdS$_{x}$Se$_{1-x}$ ($x=0.78$) nanobelts. Our results demonstrate the feasibility of this technique as an ultrasensitive time-resolved fluorescence spectrometer. © 2007 Optical Society of America

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1. INTRODUCTION

Observation of transient behavior of the excited states is of great importance and interest in studying carrier dynamics and relaxation processes of materials [1]. With upconversion [2–8] and Kerr-gating [9,10] techniques, it is possible to investigate fast dynamics of photophysical or photochemical processes proceeding on a femtosecond time scale [11,12]. Since the output wavelength and direction of the sum frequency beam are far away from those of the detected fluorescence and gating laser pulses, the upconversion technique is basically a background-free detection. The temporal profile of fluorescence is thus sensitively obtained. In this technique, however, the phase match angle of nonlinear crystal to generate the sum frequency output has to be varied for different wavelengths. As a result, the resulting spectra have to be reconstructed from the measured kinetics at each wavelength. A major drawback is that the low-frequency noise together with the long measurement time limits the quality of the obtained spectra. Only recently, by using near-IR gating and improved light-collection geometry [13], the bandwidth of the upconverted signal can be as large as 10 000 cm$^{-1}$. The recently developed Kerr-gating method for collection of time-resolved fluorescence spectrum is superior to the frequency upconversion method because of its high efficiency. In addition, the phase-matching condition is automatically satisfied at every wavelength in comparison with the upconversion technique. A typical efficiency of the Kerr technique, which is defined as the ratio between the number of the photons passing through the Kerr gate and the overall photons directed to the Kerr gate, can be up to 5–10%. The temporal resolution of the Kerr-gate method is limited by the response time of the Kerr medium, which can be up to several hundred femtoseconds [1].

It was first demonstrated by Zhang and co-workers [14] that a noncollinear optical parametric amplifier (NOPA) can be used to amplify the light pulses with an extremely low signal level of $\sim 100$ aJ per pulse for a scanned optical parametric amplification frequency-resolved optical gating (FROG), and the signal level is reduced to $0.8–0.9$ fJ per pulse for a single-shot optical parametric amplification FROG [15], which is capable of measuring a complicated transient spectrum with a single shot of the laser. It was also suggested that the NOPA technique can be applied to detect very weak fluorescence [14]. Recently, Fita and co-workers [16] have reported an experimental proof-of-principle method based on NOPA in a $\beta$-barium borate (BBO) crystal for recording femtosecond time-resolved fluorescence spectra in the visible range. More recently, Chen et al. [17] extended this technique to the infrared range by using the so-called “parametric idler-to-signal frequency upconversion technique,” in which the fluorescence in the near-IR region is injected into the NOPA as the idler seeding, and the near-IR seeding is parametrically amplified. In the meantime, it is also upconverted into the corresponding signal branch in the visible region. Such a technique solved the problem of detecting the low-level signal in the near IR with a gain as high as $10^6$ and, in principle, the detectable IR signal can be extended from the near IR to the mid-IR by selecting appropriate nonlinear crystals for NOPA.

The advantage of using an OPA is that it allows direct amplification (without changing the frequency) of the
seeding photons in the visible and near-IR range located in the frequency range of the signal branch of the OPA with a significant optical parametric gain as high as $10^6$–$10^8$ [18]. It also allows amplification of the optical pulse in the IR by seeding it in the idler branch of the OPA so that the signal in the IR can be detected in the visible through the above-mentioned parametric idler-to-signal frequency upconversion technique, and yet the gain for seeding in the idler can be even higher than that seeding in the signal branch of the OPA due to the change of quantum energy from the idler to the signal [17]. In the meantime, the bandwidth of a femtosecond OPA generally can be as broad as more than 10 000 cm$^{-1}$ covering the entire optical range from the visible to the near IR [19,20] and thus provides an ideal amplifier without spectral distortion.

In this paper, we present a detailed technique for recording femtosecond time-resolved spectra for nanosecond fluorescence based on noncollinear parametric amplification and pushing the detection limit of this technique. It has been found that the gain of the amplifier is determined to be $\sim 1.2 \times 10^6$, while the detection limit of the fluorescence amplifier can be as low as 5.1 aJ per pulse. By employing the parametric amplification method, we measured the time-resolved fluorescence spectra of Rhodamine 6G dye in ethanol, and the lifetime of the fluorescence at 580 nm was found to be 779 ps with a temporal resolution of 150 fs limited mainly by the pulse duration of the femtosecond excitation laser. Our results suggest that the time-resolved fluorescence amplifier based on NOPA is a powerful spectroscopic tool to investigate the fast dynamics of photophysical or photochemical processes proceeding on a femtosecond time scale. We also extended this technique to the samples other than laser dyes, such as the newly fabricated emissive semiconductor Cd$_x$Se$_{1-x}$ (x = 0.78) nanobelts. Our experiment found that high-quality time-resolved spectra and the decay profiles of the photoluminescence were obtained successfully, which indicates that the parametric fluorescence amplifier technique has a high sensitivity, a temporal resolution limited mainly by the pulse duration of the pumping laser, and a very broadband feature.

2. EXPERIMENTAL

The schematic of the time-resolved fluorescence amplifier based on NOPA is shown in Fig. 1. A 1 kHz Ti:sapphire regenerative amplifier (Hurricane, Spectra-Physics) produced 300 $\mu$J pulses of 150 fs duration at 800 nm. The beam’s diameter was reduced by a telescope constructed by lenses L1 (f = 200 mm) and L2 (f = −75 mm) to meet the required beam intensity for frequency doublers (SH1). The laser pulse energy was then split into two parts with a ratio of 5:1. The two beams were frequency doubled independently by two 1 mm BBO crystals. After passing through a delay line, the weaker beam (≈5 $\mu$J) was focused by lens L6 (f = 150 mm) onto a rotating sample cell to excite the fluorescent samples. The thickness of the cell is 1 mm and filled with solution of Rhodamine 6G dye in ethanol with a concentration of $\sim 5 \times 10^{-5}$ M. For the measurement of the transient fluorescence of Cd$_x$Se$_{1-x}$ (x = 0.78) nanobelts, the sample was prepared by simply dropping the nanobelts in ethanolic solution onto a glass slide and drying in the air.

A notch filter (NF) was used to remove the 800 nm residue of the 400 nm excitation beam before it was used to excite the dye, avoiding the interference caused by the 800 nm residual beam. The fluorescence was collected by lens L7 (φ = 25.4 mm, f = 38.1 mm) and then focused by lens L8 (f = 150 mm) onto a 1 mm thick BBO crystal cut at $\theta_c$ = 30°, $\phi_c$ = 0°. The size of the pump beam for the NOPA (with an energy of $\sim 120 \mu$J) was adjusted with an inverted telescope consisting of a lens pair L3 and L4 to $\sim 0.5$ mm in diameter to match the beam size of the fluorescence in the BBO crystal. A collection efficiency of the fluorescence is estimated to be $\sim 2\%$ based on the solid angle of lens L7.

3. RESULTS AND DISCUSSION

The orientation of the BBO crystal was adjusted to achieve the widest gain bandwidth accessible at the central wavelength of the fluorescence of the Rhodamine 6G. The fluorescence of the Rhodamine 6G was collected by lens L7 and then imaged onto the surface of the BBO crystal as the seeding beam. After seeding the fluorescence into the OPA and carefully overlapping the seeder with the pump beam both spatially and temporally, one can see a strong amplified bright spot near the superfluorescence ring as shown in Fig. 2. The direction of the seeding fluorescence was adjusted to match the angle of the parametric superfluorescence cone in order to achieve a maximum amplification. The amplified fluorescence was collected by an achromatic lens before it was fed into the entrance slit of a grating spectrograph equipped with a semiconductor-cooled CCD array (128HB, Acton Research). The time-resolved amplified fluorescence spectra were recorded by the CCD array.

The amplified fluorescence in the visible can be contaminated by the fluorescence background from those unamplified photons outside the gating pulse window, especially when the seeding beam is attenuated in order to find the detection limit. In addition, it can also be con-
taminated by the parametric superfluorescence beam from the BBO crystal generated by the pump beam as a superfluorescence cone shown in Fig. 2. To minimize the above-mentioned interferences, two mechanical shutters S1 and S2 were employed to block the pumping beam for the NOPA and the excitation beam for the dye, respectively. The use of two shutters helps in acquiring the integrated background from the individual interference sources. The integrated background is used for background subtraction in processing the spectra of the amplified fluorescence.

To study the kinetics of the fluorescence, a single-wavelength detection setup with a sensitivity of $10^{-5}$ in the difference of the optical density was constructed for the amplified fluorescence detection. The seeding fluorescence was chopped by a chopper with both shutters S1 and S2 being open; the amplified fluorescence was then focused onto a monochromator and was detected by a photodiode (PDA55, Thorlabs). The signal detected by the photodiode was then sent to a lock-in amplifier (Model 5210, EG&G), whose frequency was locked at the frequency of the chopper, and the time constant of the lock-in amplifier was set at 1 or 3 s, and the total time used for a single scan (1 ns) is $\sim$15 min. In this way, the interference of the superfluorescence acts as a background and thus can be reduced. Owing to the large amplification factor of the NOPA, the amplified signal is generally several orders of magnitude stronger than the unamplified fluorescence interference. In addition, the unamplified fluorescence is a long-pulsed signal while the amplified signal is an $\sim$150 fs long signal amplified by the gating pulse. Therefore, in general, the unamplified fluorescence would not interfere with the measurement since the former is much weaker than the latter. However, it would become comparable with the amplified signal when the system is used to measure the detection limit, where the seeder is attenuated by filters with an optical density ranging from 0 to 3.3, which is corresponding to an attenuation coefficient from 100% to 0.05%. In this case, the use of a lock-in amplifier can significantly reduce the interference of the background fluorescence.

The kinetics of fluorescence decay was recorded by scanning the optical delay line between the fluorescence excitation and the NOPA pump beams. Figure 3 shows the steady-state fluorescence spectrum of Rhodamine 6G, as well as the transient amplified fluorescence spectrum recorded at a time delay of 2 ps. Both spectra are normalized. It can be seen that the normalized transient fluorescence spectra reproduce the steady-state fluorescence spectrum fairly well. The data shown in Fig. 3 indicate that the spectral homogeneity of the NOPA is excellent in this spectral range since it is near the spectral center of the gain profile of the 400 nm pumped BBO-OPA, where the gain is almost independent of the wavelength. However, when the wavelength of the seeder is near the edge of the gain profile, one needs to account for the inhomogeneity of the OPA and make some necessary corrections.

Figure 4 displays the kinetic traces of the amplified fluorescence (the signal branch of the OPA) and the corresponding idler beam. The former is at the peak wavelength of the dye near 580 nm, and the latter is at the signal-to-idler parametrically converted wavelength near 1290 nm. These two kinetic processes were fitted by a mo-
noexponential decay with a time constant of 779±14 ps at the signal and 794±20 ps at the idler beam detection. Both of them are consistent with each other considering the experimental errors as indicated. These values lie within the range of the reported fluorescence lifetimes measured for Rhodamine 6G dye dissolved in ethanol [21].

To verify that there is no gain saturation in the OPA at the signal level used in our work, we measured the relation between the seeding energy and the energy of the amplified signal by attenuating the seeder with optical density filters. Figure 5(a) illustrates the relation of the intensity of the amplified signal versus the seeder intensity. The data were obtained by attenuating the intensity of the seeding fluorescence with a series of optical density filters with their optical density ranging from 0 to 3 step-by step. It was found that the intensity of the amplified signal varies linearly with that of the seeder, indicating that there is no gain saturation in the experiment. Figure 5(b) shows the normalized fluorescence decay kinetics with the seeder attenuated at various optical densities. The results are basically the same as can be seen in Fig. 5(b). These results also show that the amplification is linear and no saturation occurs in our experiment.

We also measured the gain factor of our parametric fluorescence amplifier by determining the relative integrated intensity of the amplified and unamplified fluorescence intensity over the entire decay profile by the following procedures. We first determined the amplified fluorescence decay profile by a NOPA fluorescence amplifier at a gating width of 150 fs and a given pump power of 110 μJ/pulse. It is important that the detecting photodiode is working in a linear response region. Thus an integrated relative intensity can be calculated by integrating the fluorescence decay kinetics. We then measured the relative integrated intensity of the seeding fluorescence, which was detected directly by the same photodiode, the relative integrated intensity was obtained as the peak output of the photodiode. Finally, the gain factor was derived by dividing the integrated intensity of the amplified fluorescence by that of the seeding fluorescence. The resulting gain factor of the fluorescence amplifier is $1.2 \times 10^6$.

The detection limit of the parametric fluorescence amplifier has also been obtained experimentally. With the known amplification factor at the given pumping power, the absolute seeding energy can be determined by measuring the energy of the amplified fluorescence and then dividing it by the gain factor. At a pump power of 110 mW and no attenuation of the seeder, the measured energy of the signal after amplification was 30 nJ per pulse, which is strong enough to be measured by a calibrated energy meter. Therefore, taking into account that the gain of the OPA is $1.2 \times 10^6$, the seeding fluorescence energy without any attenuation is found to be $\sim 25.4 \, \text{fJ}$ per pulse. Then, we attenuated the fluorescence intensity by a factor of 2000 or to 0.05% of its original value, which corresponds to a seeding fluorescence power of 13 aJ per pulse or 37 photons at 580 nm in particular. The attenuated fluorescence after amplification at the short time delay can still be detected as shown in Fig. 6. It is found that the effective amplitude of signal (S) is found to be 1.0, while the amplitude of the noise (N) is $0.4$, which corresponds to a signal-to-noise (S/N) ratio of 2.5. However the acquired kinetic trace can hardly reflect the fluorescence decay profile. This can be attributed to the statistical property of the emitting photons when the number of fluorescence photons approaches a single photon level within the detection time gate [22]. We assume that when the ratio of the S/N can be reduced further to 1 by attenuating the seeder intensity, the noise level remains the same. The corresponding signal level at S/N=1 is our detection limit. Since the seeding level in Fig. 6 is 13 aJ per pulse or

![Fig. 5. (a) Relation between the amplified fluorescence intensity at the signal branch and the corresponding seeder intensity at a fixed 400 nm pump power of 110 μJ per pulse. The intensity of the seeding fluorescence was attenuated from 100% to 0.1%. (b) Normalized kinetic traces with different attenuation level of the seeding fluorescence, i.e., with a transmission of 100%, 10%, and 1%, respectively.

![Fig. 6. NOPA amplified fluorescence decay kinetics with an attenuation factor of 0.05%.](image-url)
its band-edge emission can be continuously tuned from blue to red by changing the constituent stoichiometry. However, the defects and structural disorders in the crystal would lead to the trap states lying below the band edge, which gives rise to a redshift in the optical emission [24]. For the steady-state emission, spectra of CdS$_{x}$Se$_{1-x}$ are rather broad, which can hardly give an unambiguous spectral assignment. Time-resolved emission spectrum is an efficient means in differentiating the band-edge emission from the trap-state emission by providing additional information on the carrier-relaxation kinetics.

Figure 7(a) shows the transient amplified fluorescence spectrum of the CdS$_{x}$Se$_{1-x}$ nanobelt ($x = 0.78$) recorded at a time delay of 1.5 and 3.0 ps, respectively, after the 400 nm laser excitation. It clearly reveals that the time-resolved emission spectra are temporally inhomogeneous and different from that of the steady-state emission. The emission spectrum is redshifted at a later time. The corresponding fluorescence decay kinetic curve recorded with a lock-in amplifier at the maximum-intensity wavelength of 587 nm is displayed in Fig. 7(b). The curve consists of a 0.5 ps rising phase and a 2.1 ps decay phase, and it is tentatively assigned to the emission from the trap states. Further results will be reported elsewhere. The decay profile as well as the transient fluorescence spectra show a high S/N ratio, which demonstrates the superiority of this technique in the study of ultrafast carrier-relaxation processes for semiconductor nanostructured materials.

4. CONCLUSIONS

In conclusion, we have demonstrated a technique for extremely sensitive recording of femtosecond time-resolved fluorescence spectra by optical parametric amplification in a BBO crystal. A good spectral fidelity has been achieved in the measurement of fluorescence spectra of Rhodamine 6G. The gain factor of the NOPA was found to be as high as $-1.2 \times 10^6$, and the detection limit of the fluorescence amplifier was determined to be only $-5.1 \text{ A}_\text{d}$ per pulse, corresponding to 15 photons per pulse. The time-resolved kinetic process of the Rhodamine 6G is also obtained with a resolution estimated to be $-200 \text{ fs}$. The time resolution is limited mainly by the 150 fs pulse duration of the pumping laser and by the group-velocity dispersion of the pump beam, which is measured to be $-200 \text{ fs}$ by the autocorrelation technique, as it passes through the optical components in the setup. This technique promises to be a powerful tool in the study of time-resolved emission of photochemical and photophysical processes. With this technique, we have also acquired the transient fluorescence spectra as well as the fluorescence decay profile of CdS$_{x}$Se$_{1-x}$ ($x = 0.78$) nanobelts.

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