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SPECIAL TOPIC — 60th Anniversary of Department of Physics of Nanjing Normal University

Increase of photoluminescence blinking frequency of 3C–SiC nanocrystals with excitation power*

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Super-resolution optical fluctuation imaging is dependent on the blinking frequency of fluorophores. Consequently, improvement of the photoluminescence (PL) blink frequency is important. This is achieved for 3C–SiC nanocrystals (NCs) by simply increasing the excitation power. Using an excitation of 488 nm with powers of 5 μW to 50 μW, individual 3C–SiC NC always exhibits PL blinking with a short on-state sojourn time (< 0.1 s). A fast Fourier transform method is exploited to determine the PL switching frequency. It is found that the frequency of the bright state increases from 2 Hz to 20 Hz as the excitation power increases from 5 μW to 50 μW, which is explained by the Auger photonionization model.

Keywords: photoluminescence, nanocrystals, blinking, Auger photonionization

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1. Introduction

It is well-known that many types of fluorophores, such as single molecules,[1] fluorescent proteins,[2] polymer segments,[3] semiconductor nanoparticles,[4,5] nanorods,[6] and nanowires,[7] exhibit fluorescence intermittency;[8] *i.e.*, the photoluminescence (PL) of the fluorophores are seen to randomly flicker between emitting ("on") and almost dark ("off") periods under continuous excitation conditions. This phenomenon is usually called PL blinking.[9] In the case of light-emitting devices, fluorescence intermittency results in a lower quantum yield, and PL blinking is generally considered to be undesirable for conventional bioimaging or biosensing applications. This happens because fluorescence intermittency leads to a periodic loss of the of the tracking signal. Thus, much effort has been devoted to suppressing PL blinking.[10–15] However, PL blinking has revolutionized super-resolution microscopy.[16–20]

Super-resolution optical fluctuation imaging (SOFI) is a stochastic method based on PL blinking of fluorophores.[16] This method involves the higher-order statistical analysis of temporal fluorescence fluctuations recorded in a sequence of images. A fundamental assumption is that the different emitters independently switch between states in a stochastic way. The limited optical resolution of conventional fluorescent imaging techniques is attributed to the signal superposition of the fluorescence signal originating from different neighboring emitters. The n-th order cumulant (a quantity related to the n-th order correlation function) filters this signal based on its fluctuations such that only highly correlated fluctuations are retained by refining the allocation of the emitters. Specifically, the remitting signal is limited to emitters associated with a particular pixel in a detector. The fluorescence signal contribution to nearby pixels yields lower correlation values after n-th order cumulant in a nonlinear manner, which allows closely spaced emitters to be distinguished. Consequently, the width of the point spread function (PSF) is reduced by a factor of $\sqrt{n}$, resulting in a significantly improved resolution. This method relies on higher-order statistical analysis of fluorescence blinking. In fact, if the on state/off states last for long periods of time, then the limited measurement times will lead to a 'correlation' noise in SOFI. Therefore, frequent switching between emissive/dark states is highly desirable in this procedure.

Silicon carbide (SiC) is an important semiconductor, which has exhibited great potential in a wide range of applications.[21–23] The PL blinking of SiC was discovered by Castelletto *et al.*,[24] which suggests that SiC is a potential single-photon source. This behavior was ascribed to the emission of an intrinsic defect, known as the carbon antisite–vacancy pair. Subsequently, PL blinking effects of a single 3C–SiC nanocrystal (NC) were investigated by Gan *et al.*,[25] and the results implied that it can be used as a fluorophore for SOFI. In this work, the excitation power density-dependent steady-state fluorescence and PL blinking of a single 3C–SiC NC are studied. It is determined that the on-state sojourn

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time is usually as short as several time frames under specified conditions. Moreover, as the excitation power increases, the switching frequency between emissive/dark states and on-state substantially increase.

2. Experimental section

The preparation procedure for the 3C–SiC NCs can be found elsewhere.[25] Commercial 3C–SiC powder (Alfa Aesar Co., Inc.) with a grain size of several micrometers was used as the precursor. Approximately 6.0 g of the micro-powder was etched at 100 °C for 1 h in a solution composed of 15 mL of 65-wt% nitric acid (HNO_3) and 45 mL of 40-wt% hydrofluoric acid (HF). After the resulting solution was cooled, centrifugation was performed at 8000 rpm for 5 min to remove any excess acid. Subsequently, the powder obtained was washed with deionized water and dried at 70 °C in an oven. The powder was then re-dispersed using 30 mL of deionized water, followed by ultrasonic treatment for approximately 60 min. The supernatant containing 3C–SiC NCs was finally obtained by centrifugation at 8000 rpm for 10 min. Further structural characterization can also be found in a previous report.[25]

The optical absorption spectrum was obtained using a Shimadzu UV-2600 spectrometer. Ensemble PL measurements were performed on an FS5 PL spectrometer (Edinburgh Instruments). For single NC fluorescence measurements, the suspension with 3C–SiC NCs was diluted to approximately 1 nM and ultrasonically treated for one hour to individually disperse the NCs. Subsequently, a 5-μL portion was spin-coated onto a glass slide. After drying, a coverslip was placed over the glass slide and the sample was transferred and mounted on a microscope. Spatial scanning PL images were acquired using a confocal microscope (LSM780, Carl Zeiss) equipped with a spectral window of 2.9 nm and a CCD camera. The microscope setup was also used to observe and record the fluorescence trajectories of the 3C–SiC NCs.

3. Results and discussion

The 3C–SiC NCs with sizes ranging from 2 nm to 6 nm (most probable size of ∼3.8 nm) were synthesized by a chemical corrosion method (see previous report).[25] Most of the particles are close to or smaller than the extonic Bohr radius R (2.7 nm),[26] thus evident quantum confinement effect is expected. The bandgap of the as-prepared 3C–SiC NCs was estimated from the absorption spectrum of the corresponding aqueous solution, according to the Kubelka–Munk (KM) function. As shown in Fig. 1(a) and inset, the bandgap is approximately 2.32 eV, which is slightly larger than $E_g = 2.2$ eV of the bulk 3C–SiC material.[26]

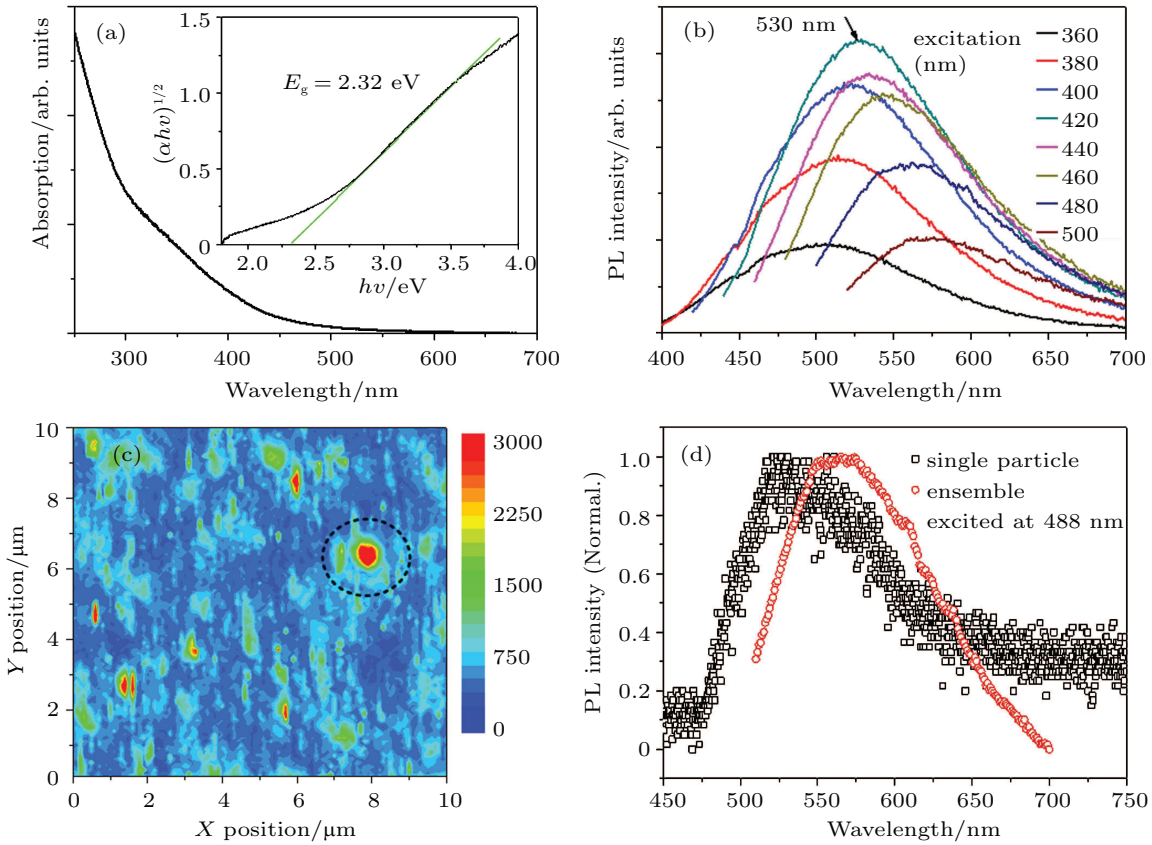


Fig. 1. (color online) (a) Absorption spectrum of 3C–SiC NC aqueous solution, inset: a conversion based on the KM function. (b) Collective PL spectra of 3C–SiC NC aqueous solution excited at different wavelengths. (c) Confocal scanning PL image of single 3C–SiC NCs. The brightest intensity is highlighted by a circle. The scanning increment is 100 nm. (d) Comparison of PL spectra from ensemble NCs in aqueous solution (red circles) and individual NC on a microscope slide (black squares).

The ensemble PL spectra of the 3C–SiC NCs dispersed in an aqueous solution is shown in Fig. 1(b). The emission red-shifts as the excitation wavelength increases, which is caused by the quantum confinement effect, as revealed previously.[26] The strongest emission peak appears at 530 nm at an excitation of 420 nm. The maximum PL peak position corresponds to a bandgap of 2.34 eV, which is consistent with the absorption band edge. Figure 1(c) shows the spatial scanning PL image of several individual SiC NCs with excitation at 488 nm using an Ar ion laser, where the brightest intensity is highlighted with a black circle and the PL spectrum of the brightest NC is shown in Fig. 1(d). A red-shift is observed in the emission peak of the collective NCs (black squares) in comparison with that of an individual NC (red circles) under the same excitation (Fig. 1(d)). This is possibly due to the dipole–dipole interactions between neighboring NCs in the ensemble PL.[27]

The single-particle PL spectra of the SiC NC excited at different powers were recorded. When the Ar ion laser power was increased from 10 μW to 50 μW, the PL intensity gradually increased without any apparent changes in the peak position and spectral shape (Fig. 2(a)). The relationship between the excitation power density and the integrated single-particle PL intensity is plotted in Fig. 2(b). The linear dependence indicates that the emission of SiC NC is dominated by simple free-exciton transition without a high-order nonlinear optical response. It also suggests that structural destruction was not induced by the laser within the power range of 10 μW–50 μW.

The PL time trajectory of the single SiC NC is recorded to investigate the PL blinking. A total of 4.2×10^4 frames were acquired with a time bin of 10 ms for each excitation power. All the measurements illustrated in Fig. 3 were from a single SiC NC. As shown, its on-state sojourn time is very short, primarily shorter than 10 bin times (0.1 s), and the appearance of the on-state is rare. The SiC NC is predominated by the off-state with sparse on-state events, which is in good agreement with previous work.[25] According to the model proposed by Efros and Rosen,[28] the NCs are thought to undergo Auger ionization through photoexcitation. In that case, a doubly excited NC expels an electron out of the core using the recombination energy of the alternative exciton. The electron is then ejected from the NC and occupy the surface trap state, leaving a hole in the NC. Consequently, this causes the subsequent photo-generated excitation form positive trions to undergo nonradiative recombination. The NC will not emit until it is neutralized. For the chemical SiC NCs derived from corrosion without any passivation, there are a large number of Si- or C-terminated unsaturated dangling bonds at the surface that form trap states for electrons.[29] Therefore, the emission of SiC NCs is preferentially quenched by surface trapping, resulting in dark states.

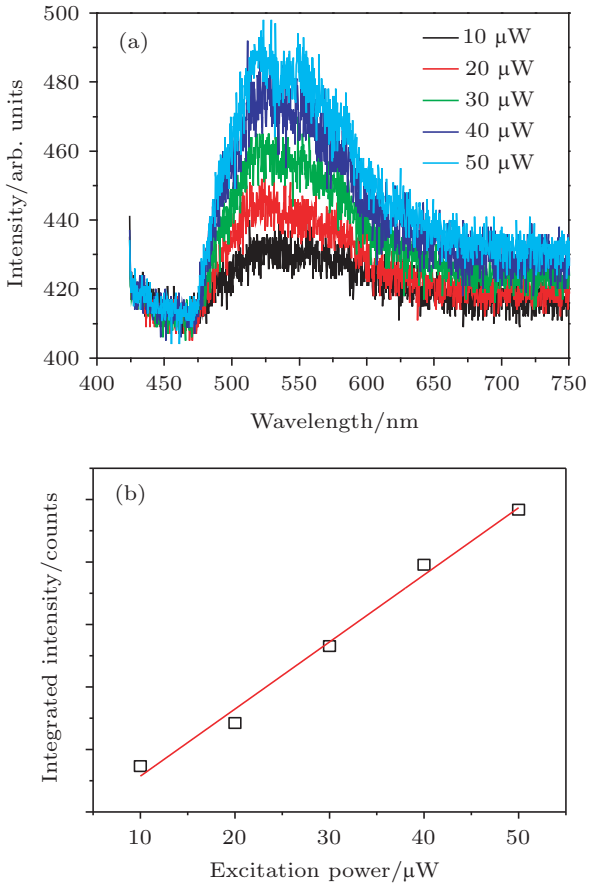


Fig. 2. (color online) (a) PL spectra measured as a function of the laser excitation powers for an individual 3C–SiC NC. (b) The relationship between integrated PL intensities and excitation powers fitted using a linear function.

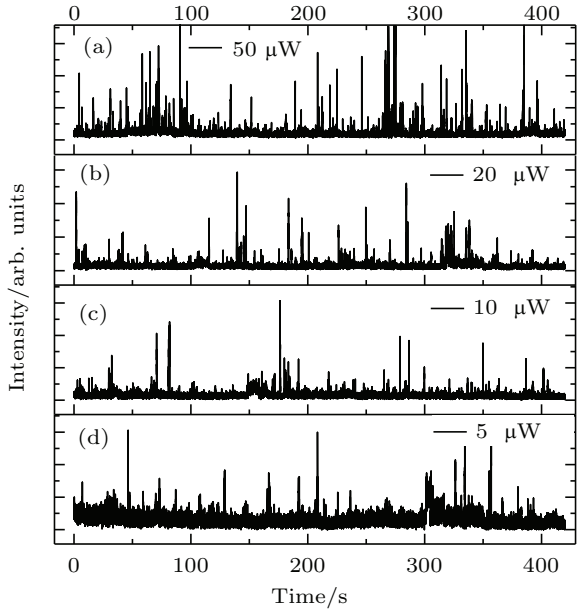


Fig. 3. PL time trajectories for the same single 3C–SiC under four different excitation powers. (a) 50, (b) 20, (c) 10, and (d) 5 μW.

Interestingly, based on the observations from Fig. 3(a) to Fig. 3(d), the appearance of the on-state becomes much rarer when the excitation power decreases from 50 μW to 5 μW. In conventional studies, the on/off state distributions are usually measured by the statistic of the occurrence of each associated

intensity. However, as shown in Figs. 4(a) and 4(b), the occurrence of PL blinking from the entire PL time trajectory shows indiscernible separation of on/off states, because the on-states are weak, scarce, and short-lived. Nevertheless, the histograms can be divided into two components through numerical fitting so that the occurrence ratio of on/off states can be acquired under constraint. The proportions of on states are 27.5% and 36.1% for excitation powers of 5 μW and 50 μW, respectively. These statistics partially indicate that more bright states appear when the excitation power increases but they fail to directly describe the switching frequency between on- and off-states. Indeed, the information on the occurrence of on-state event is embedded in the results shown in Figs. 4(a) and 4(b), which is composed of both repetitions and the sojourn time of the on-state events. In other words, when the on-state sojourn time is very long but the corresponding switch-on frequency is very low, then the accumulated occurrence could be considerable. It is well known that the dwell time probability distribution, dwell time (t) *versus* the probability $(p(t))$, follows a power law.[25,30] Therefore, the on/off switching frequency cannot be determined by simple statistic of on-state occurrence.

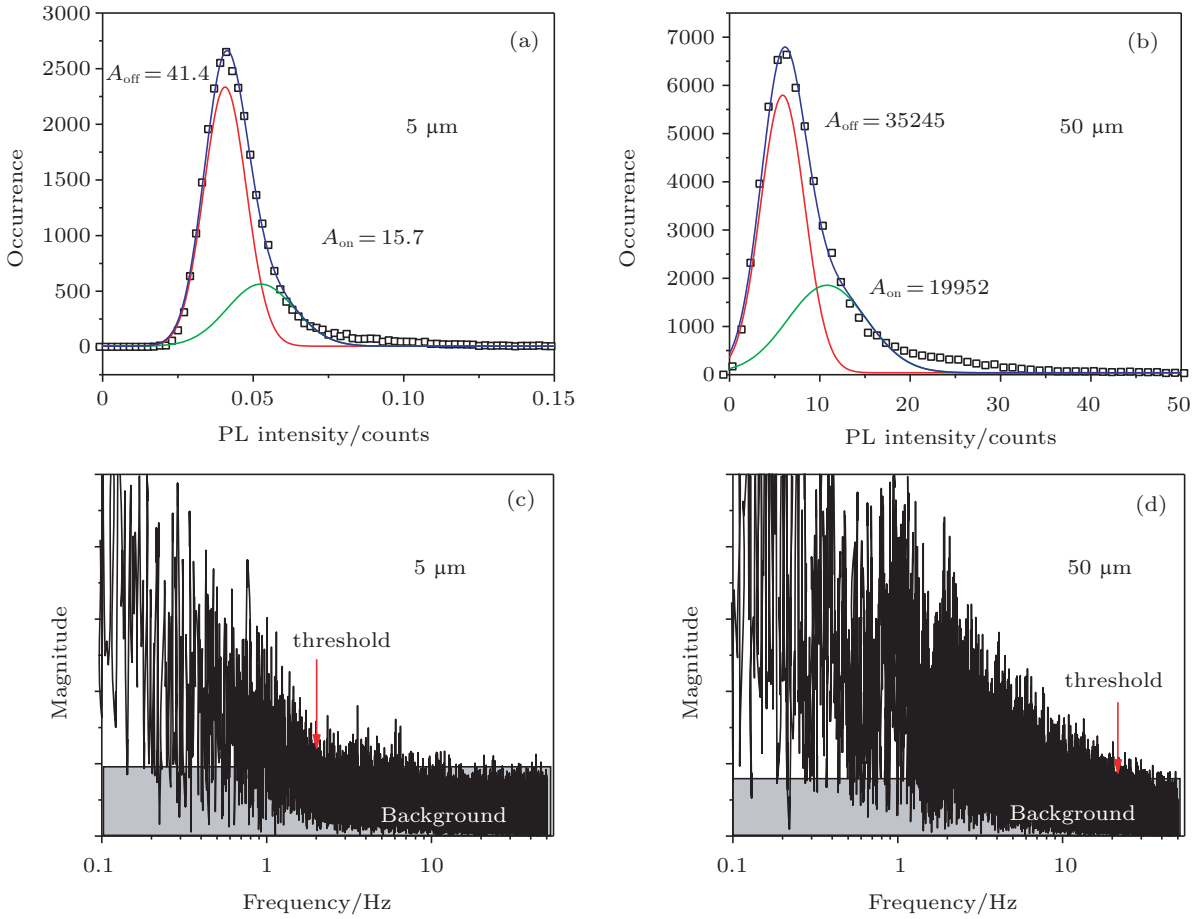


Fig. 4. (color online) (a) and (b) Intensity statistics for PL time trajectories recorded for two different excitation powers corresponding to Fig. 3(d) (5 μW) and 3(a) (50 μW). The experimental results are fitted by two Gaussian peaks that are ascribed to the on- and off-states. (c) and (d) Fast Fourier transform (FFT) spectra of the PL time trajectories under excitation powers of 5 μW and 50 μW.

To directly investigate the switching frequency, a fast Fourier transform (FFT) was performed on the PL time trajectories for excitation powers of 5 μW and 50 μW. The relationship between the signal magnitude and the appearance frequency is then acquired. The lowest magnitude at the highest frequency is regarded as the background (dark state) because the intensity of the dark state is equal to that of the noise and occurs most frequently. The background is marked by the shadow rectangle. Thus, the signal that appears above the shadow rectangle can be regarded as a bright state. As shown in Fig. 4(c), when the excitation power is 5 μW, there is a terrace at the high-frequency side. In this case, the threshold occurs at a frequency of ∼2 Hz, which implies that the frequency of the signal with a magnitude above the noise is below 2 Hz. Whereas, when the excitation power is increased to 50 μW, the background region is compressed to the high-frequency edge, and the frequency of the bright states increases to approximately 20 Hz (Fig. 4(d)). The FFT results confirm that the PL of 3C–SiC NCs blinks more frequently at a higher excitation power, which is consistent with the intuitive observation. As stated in the introduction, the switching of emissive/dark states at high frequency is greatly beneficial to SOFI.

The photo-physics associated with the experimental observation are tentatively explained by attributing the PL blinking to Auger photon-ionization.[25,28,30] The PL is turned off by ejecting an electron to the surface trap via a double excitation. Apparently, as the excitation intensity increases, double excitation of a single NC becomes easier, which promotes Auger photon-ionization. Meanwhile, PL is switched on after the return of the ejected electron, which also requires energy transfer from the excited states. At a higher excitation intensity, the sojourn of an ejected electron at the surface, the dark state dwell time also becomes shorter. Therefore, a high excitation power facilitates the on-and-off switching process, causing the PL of 3C–SiC NCs to blink more frequently.

4. Conclusion

In summary, PL blinking at a high frequency is very important for super-resolution optical fluctuation imaging. In this work, 3C–SiC NCs with green emission was fabricated. Under 488-nm laser excitation with powers of 5 μW to 50 μW, the individual 3C–SiC NC exhibits PL blinking with a short on-state sojourn time (< 0.1 s). Conventional statistics on the occurrence of the on/off states suggest that the proportion of on states are 27.5% and 36.1% for excitation powers of 5 μW and 50 μW, respectively. Moreover, a straightforward fast Fourier transform method was developed to determine the PL switching frequency. The results verify that the frequency of the on-state increases from 2 Hz to 20 Hz, when the excitation power increases from 5 μW to 50 μW. Moreover, the PL can be modulated by various effects, such as photonic crystal and surface plasmon.[31,32] Additional approaches for controlling PL blinking will be developed in the future.

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