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Citation: Applied Physics Letters **85**, 5514 (2004); doi: 10.1063/1.1829392
View online: http://dx.doi.org/10.1063/1.1829392
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/85/23?ver=pdfcov
Published by the AIP Publishing

Two-photon-induced photoenhancement of densely packed CdSe/ZnSe/ZnS nanocrystal solids and its application to multilayer optical data storage

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(Received 6 July 2004; accepted 4 October 2004)

We report on a two-photon absorption-induced photoenhancement effect on a densely packed CdSe/ZnSe/ZnS core-shell semiconductor nanocrystal solid film. The enhancement is found to be irreversible without a noticeable blueshift in emission spectra, hence we attribute the enhancement to the photoannealing of interface defects rather than to the photo-oxidation or surface passivation by other molecules. The two-photon enhancement allows us to record the enhanced spots three dimensionally, hence demonstrating the feasibility of its application to multilayered optical data storage based on nanocrystal solids. © *2004 American Institute of Physics*.
[DOI: 10.1063/1.1829392]

Semiconductor nanocrystals (NCs) have been receiving much attention in the fields of physics, chemistry, and biology due to their attractive optical properties such as narrow emission bands, the emission wavelength tunability with size and the photostability.[1,2] Their potential applications span from optoelectronic devices to fluorescent labels in biology and quantum computing. At the center of such an enormous potential is its efficient and enhanced brightness. In that respect, recent observations of the luminescence enhancement of NCs in both solution and solid states[3–7] upon irradiation with above-band-gap energy photons have brought much interest from the community.

Previous studies reported up to an order of magnitude higher enhancement upon irradiation. The enhancement effect is thought to be caused by either photoinduced surface chemistry which rids the surface defect states,[3,6,7] or photophysical processes such as annealing of the defect states and stacking faults.[4,5] While the photochemical process is commonly an environment-dependent, reversible process, the annealing effect causes a permanent enhancement regardless of the nanocrystal environment, which could be applied to optoelectronic applications. It is our interest here to apply the photoenhancement of a densely packed NC solid to multilayered optical data storage.[8,9]

The important requirement for multilayered optical data storage is ability to excite the recording material using multiphoton absorption, such as two-photon excitation (2PE). 2PE with an infrared (IR) laser beam should be capable of inducing luminescence enhancement only in the region near a diffraction limited focal spot inside the NC solid, thereby enabling the recording of enhanced spots three-dimensionally. Furthermore, the enhancement characteristics in NCs at the surface of the solid and inside the solid could also be probed with the penetrating IR excitation wavelengths.

Until now, the luminescence enhancement due to 2PE has not been studied. In this letter, we demonstrate the 2PE induced enhancement effect on densely packed NC solid films and subsequently, its application to multilayered optical data storage. In particular, we use doubly coated core-shell NCs (CdSe/ZnSe/ZnS) for this application. The doubly coated core-shell NCs provide improved photostability, enabling signal contrast to be maintained for months after recording.

A typical synthesis route of CdSe NCs doubly coated with ZnSe and ZnS shells is as follows. CdO, oleic acid, and octadecene (ODE) are heated together to form cadmium oleate, and then a mixture of selenium, trioctyl phosphine (TOP), trimethylpentylphosphinic acid, and ODE were swiftly injected into the stirring reaction mixture. The nanocrystals were allowed to grow for 5 min. The resulting CdSe nanocrystals were then washed and redispersed in a mixture of ODE, hexadecyl amine (HDA), trioctyl phosphineoxide (TOPO), and TOP. In accordance with volume calculations and bulk densities a primary 1 nm layer of ZnSe was deposited using zinc stearate and trioctylphosphine selenide, and an additional 1.5 nm layer of ZnS was grown using diethyl zinc and hexamethyldisilylthiane. The particles were then annealed, washed, and finally dispersed in pure chloroform. The first exciton transition peak was at ~570 nm and its emission peak at ~590 nm.

Droplets of the concentrated sample (10^{-5} M) were dried onto a coverslip glass which created a densely packed NC solid film of volume $\sim 10^8\ \mu m^3$. Under a confocal microscope, the densely packed film showed a homogeneous emission response spanning across the 5 mm × 5 mm dried region.

The two-photon fluorescence emission of nanocrystals was excited with a titanium:sapphire ultrashort pulsed laser (Spectra-Physics Tsunami) operating at a pulse width of ~100 fs, a repetition rate of 80 MHz, and a wavelength range of 800–1000 nm. The multiphoton excited fluorescence from the focus of a high numerical-aperture objective lens (NA 1.4) was collected by the same objective, and then refocused to a spectrometer with a CCD detection for spectrum acquisition, or to a photomultiplier tube (PMT) for imaging.[10]

The two-photon induced enhancement is shown in Fig. 1. The illuminated spots of NC solid are later imaged with the PMT and are shown to be enhanced by more than an

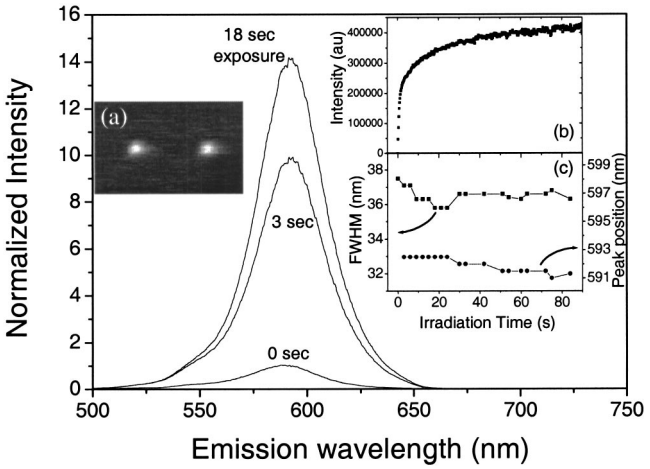

FIG. 1. Emission spectrum of the 5 nm (core) CdSe/ZnSe/ZnS NC solid upon 800 nm pulsed laser irradiation, demonstrating the 2PE induced photoenhancement. Intensity 1 MW/cm^2; insets: (a) PMT image of photoenhanced spots on NC solid; distance between the spots: 5 μm, 500 ms exposure; (b) typical time traces of the 2PE enhancement, 0.7 MW/cm^2; (c) spectral evolution of the trace shown in (b).

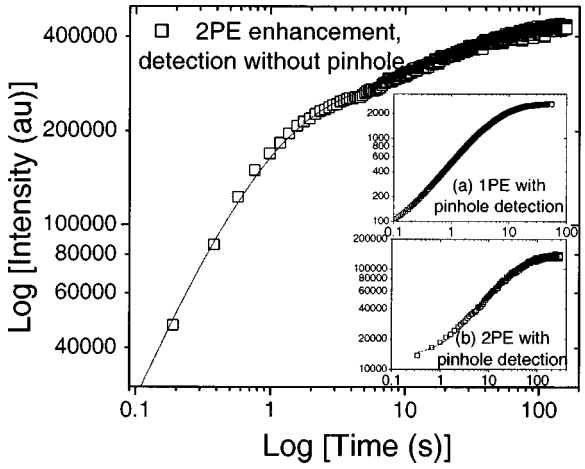

FIG. 2. Log–log plot of the time trace of 2PE induced enhancement of the sample shown in Fig. 1(b), detection without a pinhole. The solid line is a double exponential rise fit. Insets: (a) time trace of the 1PE enhancement of the same sample, 488 nm, Ar+cw laser 1 kW/cm^2; (b) time trace of the 2PE enhancement [the same condition as Fig. 1(b)], detection with a pinhole (pinhole radius 50 μm). Solid lines in insets are fits to the single exponential rise model in Eq. (1).

order of magnitude over the emission from the unirradiated area [Fig. 1(a)]. The temporal change in the emission spectrum from the infrared laser focused spot is monitored and recorded with a spectrometer [Fig. 1(b)]. Their emission spectrum shows a minimal blueshift in the first 20 s of enhancement, during which almost 90% of the total enhancement takes place. After that, there is a slight blue shift of less than 1 nm [Fig. 1(c)]. The corresponding kinetics of full width at half-maximum (FWHM) shows just a slight reduction ($\sim$2 nm) in the first 20 s; thereafter, there is only a minimal change. Once recorded, the spot remains stable under room light or in the dark. There was no loss in the signal enhancement after seven days. This demonstrates that the current enhancement is an irreversible process.

In an enhancement due to photochemical processes at the surface, it is thought that the oxygen and water molecules act as a surface adsorbant or oxidant which passivates the remaining surface states, hence resulting in a reversible, large blueshifted (peak wavelength changes more than 10 nm) enhancement.[3,6,7] However, current results show neither of these phenomena. Furthermore, the previous report[7] on core-shell NC enhancement showed much slower kinetics compared to the case of core NCs, indicating that the shell critically slows down such photochemical enhancement process. In the current case where we have used a doubly coated shell of thickness $\sim$2.5 nm to passivate the core NC, the possibility of oxygen or water molecule penetration into the core is further diminished, and hence the photochemical enhancement is believed to take a minor role in the current process.

At present, a photoinduced physical process such as annealing of the stacking fault at the interface between a core and a shell is the likely mechanism for the observed enhancement.[4,5] The interface between a core and a shell is expected to possess many stacking faults, which create defect states that quench the radiative recombination. When a high-energy electron-hole pair is created by 2PE, the resultant phonon generation can lead to a bond rearrangement which eliminates the stacking faults and defect states.[11] Such a process does not require the emission peak to blue-shift and also explains the irreversible enhancement.

The enhancement kinetics of the 2PE enhancement were studied, and its comparison with the single photon (1PE) enhancement is presented in Fig. 2. The difference in kinetics is best manifested in a log–log plot. Note that the 2PE enhancement has two linear regions in rise before reaching the maximum, whereas the 1PE enhancement shows only one linear region [Fig. 2(a)]. The 2PE kinetics is best-fitted with a double exponential rise, while the 1PE kinetic can be fitted with a single exponential rise. Such enhancement shapes were observed universally, regardless of the input power or the region. The two different rates of the enhancement (i.e., fast and slow rates) in the 2PE enhancement were caused by the enhancement at the diffraction-limited spot and at the side-lobes of the spot, respectively. In the 1PE enhancement, confocal geometry allows the placement of a pinhole which discriminates the fluorescence resulting from the sidelobes; hence only the enhancement at the diffraction limited spot is observed,[12] i.e., one rate enhancement. However, in the 2PE enhancement, the pinhole is removed due to its intrinsic confocal nature; hence the enhancement resulting from the sidelobes irradiation is also detected. The intensity of sidelobes is $\sim$10% of the peak intensity, and hence contributes to the enhancement at a slower rate. Such a double rate enhancement in 2PE could be eliminated by placing a pinhole in the detection path, in which case the enhancement shape shows only one rate of rise [i.e., a single exponential rise, Fig. 2(b)], similar to the 1PE case.

A phenomenological rate equation for the enhancement had been suggested by discriminating dark and bright NCs.[13] If the luminescence is assumed to be proportional to the number of photoannealed NCs, then a rate equation can be written as

$$\frac{dn_1}{dt} = kI^n(N - n_1), \tag{1}$$

where n_1 is the number of photon-annealed NCs, N is the total number of NCs in the irradiated volume, I is the intensity, n is the power index for an n-photon process, and k is a rate constant. Solving the equation for n_1 provides a single

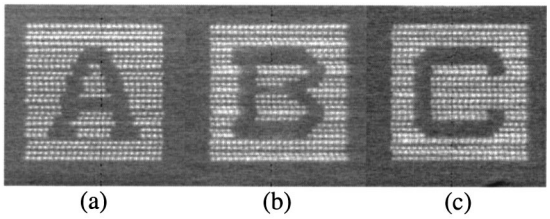

FIG. 3. 30 μm$\times$30 μm images demonstrating the multilayer recording by the 2PE induced enhancement in the NC solid film. Dot spacing 1 μm, layer spacing 4 μm, power 5 MW/cm^2, exposure time 10 ms per dot.

rate enhancement kinetics (i.e., a single exponential rise), which shows a good agreement with both 1PE and 2PE enhancements in Figs. 2(a) and 2(b), respectively.

The feasibility of the 2PE enhancement as a read-only multilayered data recording method is demonstrated in Fig. 3. The first letter A is recorded and then subsequent letters recorded with a layer spacing of 4 μm. The intensity of the recording beam was $\sim$5 MW/cm^2 at the focus, with the exposure time of 10 ms. For reading, one order of magnitude lower power was used. The exposed region produces a contrast enhancement of 300% compared with the unexposed region, but the enhancement could be further optimized with a higher intensity and slower recording.

As stated earlier, the recorded pattern is found to be stable. We kept the recorded pattern under ambient room light and in the dark condition for seven days, but found no sign of contrast degradation of the recorded patterns after the aging. The data could be erased by scanning the recorded area for a long period of time. Consequently, the reading beam must be kept at significantly lower power than the recording beam power. Typically, with a reading power of less than a tenth of the recording beam, and with a scanning speed of 1 mm/s, we could read more than two hundred times before starting to see the contrast degradation. Further experiments using different recording and reading beam wavelengths suggest that the number of read cycles could be increased by more than an order of magnitude.

In conclusion, we have demonstrated the 2PE induced photoenhancement effect on a densely packed CdSe/ZnSe/ZnS NC solid film. The enhancement is found to be irreversible without noticeable blueshift in emission spectrum. Hence we attribute the enhancement mechanism to photoannealing of interface defects rather than to oxidation of surface molecules or scavengers. The 2PE enhancement allows us to record the enhanced spots three-dimensionally, demonstrating optical data storage based on NC solids.

The authors acknowledge the support from the Australian Research Council.

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