Optics Communications 383 (2017) 555–560

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

Temperature-dependent spontaneous emission of PbS quantum dots inside photonic nanostructures at telecommunication wavelength

Muhammad Danang Birowosuto[a,b,c,d,*], Masato Takiguchi[b,c], Aurelien Olivier[a], Landobasa Y. Tobing[e], Eiichi Kuramochi[b,c], Atsushi Yokoo[b,c], Wang Hong[e], Masaya Notomi[b,c]

[a] *CINTRA UMI CNRS/NTU/THALES 3288, Research Techno Plaza50 Nanyang Drive, Border X Block, Level 6, Singapore 637553, Singapore*
[b] *NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya Atsugi, Kanagawa 243-0198, Japan*
[c] *NTT Nanophotonics Center, NTT Corporation, 3-1 Morinosato Wakamiya Atsugi, Kanagawa 243-0198, Japan*
[d] *Physics Research Center, The Indonesian Institute of Sciences, Puspitek, Serpong, Banten 15314, Indonesia*
[e] *School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*

ARTICLE INFO

Keywords:
Spontaneous emission
PbS
Quantum dots
Decay time
Nanophotonics

ABSTRACT

Spontaneous emission of PbS quantum dots (QDs) in different photonic nanostructures has been studied. We use the temperature-dependent exciton photoluminescence and the classic dipole near interface models to understand the spontaneous emission control at various temperatures. Then, we demonstrate that the enhancement and the inhibition of PbS QDs due to the local density of states (LDOS) inside nanostructures are more efficient at temperature as low as 77 K than the inhibition at 300 K. Largest emission rate enhancement at 77 K of 1.67 ± 0.10 and inhibition factors at 100 K of 2.27 ± 0.15 are reported for the gold (Au) planar mirror and silicon (Si) two-dimensional photonic crystal bandgap, respectively. We attribute those enhancement and inhibition to the large quantum yields Q_e at low temperatures, which is much larger than that at 300 K. These results are relevant for application and optimization of PbS QDs in nanophotonics at telecommunication wavelength.

1. Introduction

Lead Sulfide (PbS) quantum dots (QDs) have emerged as one of the most promising new materials thanks to its optical [1,2] and electronic properties [3]. They are actively studied due to their potential impact on recent and future technologies including telecommunication-wavelength optoelectronics [4–6] and enhanced solar energy conversion through multiple exciton upon absorption of single photon [7,8]. Regarding their emission, PbS QDs exhibit size-tunable emission in the near-infrared with high photoluminescence (PL) quantum yields and long exciton radiative decay times [1]. With those attractive properties, PbS QDs were often used as an active emitter for a coupling with silicon(Si)-based nanophotonic devices designed to operate at telecommunication wavelength [9,10].

Two earliest experiments on the weak coupling between PbS QDs and the two-dimensional Si photonic crystal (PhC) nanocavities at room temperature (RT) were demonstrated almost a decade ago [11,12]. Then, since they proved to be bright, PbS QDs in a solution were used as major probes in a rewritable Si-based PhC nanocavity [13] and the plasmonic metamaterial mode at specific polarization [14]. From all experiments, only two observations reported the spontaneous emission control rate of PbS QDs inside the photonic nanostructures. One is from the coupling of the PbS QDs and Si-microdisks [15] and the other one is from the immersion of PbS QDs solution to a three-dimensional Si PhC, which corresponds to the large-ten-fold inhibition of the spontaneous emission rates in the three-dimensional photonic bandgap [16].

Although they are many observations of the coupling PbS QDs and photonic nanostructures, there is still a question about the relationship of the spontaneous emission control, the radiative decay times, and the quantum yields of PbS QDs. The radiative decay times for PbS QDs were reported with large variations of values due to the size, the ligand, and the environment [1,2,16,17]. One report shows confidently that the decay time at RT of 5.3-nm-diameter PbS QDs inside the solution to be 500 ns [16]. However, the quantum yield Q_e of PbS QDs is not clear so that the maximum spontaneous emission inhibition through the local density of optical states (LDOS) is quantitatively unknown. We note that there is a relation between the temperatures and the quantum yields of the emitter through the thermal quenching. The emission enhancement can be strongly affected by the temperatures in

---

[*] Corresponding author at: CINTRA UMI CNRS/NTU/THALES 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Level 6, Singapore 637553, Singapore.
E-mail address: mbirowosuto@ntu.edu.sg (M.D. Birowosuto).

http://dx.doi.org/10.1016/j.optcom.2016.09.059
Received 27 July 2016; Received in revised form 16 September 2016; Accepted 28 September 2016

which the large enhancements commonly happen at low temperatures [18].

In this paper, we investigate the intrinsic emission properties of 5.3-nm-diameter PbS QDs such as decay times, splitting energies of dark and bright states ΔE, and Q_e. The decay times of PbS QDs at 300 and 77 K are 110 ± 10 and 370 ± 10 ns, respectively. Using the temperature dependences of decay times and intensities, we obtain a ΔE of 26.6 meV, which is a typical value for PbS QD [2,17,19], and a Q_e at 300 and 77 K of 0.37 ± 0.05 and 0.61 ± 0.07, respectively. The control of the emission rates of PbS QDs is obtained by placing QDs at the different distances near gold (Au) interface through different thicknesses of SiO_2 intermediate layer. At the same position of PbS QDs, the quantum yield of the QD is controlled through varying the temperatures. The largest enhancement of 1.67 ± 0.10 is reported for QDs at a distance of 20 nm from Au interface and at 77 K. Finally, we use the PbS QD emission to probe the LDOS on two-dimensional Si PhC bandgap with a lattice constant of 400 nm, a hole radius of 100 nm and a thickness of 200 nm. At 77 K, the emission rate of PbS QDs inside the bandgap is inhibited by a factor of 2.27 ± 0.15.

2. Experiments and discussions

In this section, we will analyze and discuss PL and time-resolved emission measurements of PbS QDs in polymer reference, multilayer planar, and PhC samples. For the experiments, we used a standard microPL setup. We performed a free space technique with the excitation path and the emission collection from the top using a near-infrared microscope objective as explained in Refs. [20,21]. The QDs were excited with continuous wave laser at 980 nm or short laser pulses at 640 nm while their beam spot sizes are ~3 μm [21]. The imaging parts contained two CCD cameras working from visible to short infrared wavelengths. To measure the PL spectrum, we directed the emission to a grating spectrometer with a cooled InGaAs array. For the time-resolved emission, we filtered the emission with long-pass (>1319 nm) and band-pass (1400 ± 50 nm) filters and directed it to Hamamatsu Photomultiplier (PMT).

2.1. Quantum yields of PbS QDs

Before we coupled the PbS QDs with nanostructures, we first measured the intrinsic emission properties of PbS QDs in polymer matrix reference. For this measurement, a solution of PbS QDs and (Poly)vinyl Alcohol (PVA) was spincoated on the SiO_2 top layer of Si substrate following by the deposition of a thick solution of (Poly)methyl Methacrylate (PMMA) on top of the PbS-QDs layer as a refractive-index-matching layer [22,23]. The PbS QDs were organically stabilized with oleic acid cappings and diluted with the PVA so that the volume concentration is about 1%. This is quite close with the optimum concentration of 2% for the maximum PL enhancements of PbS QDs in Si-based photonic resonators [24]. These commercial PbS QDs with a diameter of 5.3 ± 0.5 nm and an emission wavelength peak of about 1400 nm already demonstrated a high Q_e as they were able to probe the large inhibition in three-dimensional Si PhC at telecom wavelength [16]. Fig. 1a exhibits PL spectra of PbS QDs in the reference sample as a function of the temperature. We observe a strong intensity quenching in the PL spectrum at 300 K. Besides that, the emission peak shifts of about 50 nm towards shorter wavelength from a peak of 1400 nm at 4 K as the temperature increases. In addition, we observe a peak shoulder around 1570 nm in the PL spectrum at 4 K and it disappears following the temperature increase. Although they are reports for trap states existing on the QD surfaces [25,26], the origin of this peak shoulder is still inconclusive as it only presents at 4 K. This peak position shift was already observed previously and it reflects a reduction in the PbS QD energy band gap; i.e. the energy of the lowest allowed exciton state [17]. The quenching in the PL spectra at higher temperatures is accompanied by the shortening of the decay curves as shown in Fig. 1b. For the analysis, the decay curves were fitted with a double exponential with the following equation:

$$N(t) = N_1(0)\exp\left(\frac{-t}{\tau_1}\right) + N_2(0)\exp\left(\frac{-t}{\tau_2}\right) \tag{1}$$

where $N(t)$ is the total number of population from all emission channels after t time. $N_1(0)$ and $N_2(0)$ are the initial population at t=0, which have emission decay times for fast and slow emission channels of τ_1 and τ_2, respectively. The decay time average $\langle\tau\rangle$ derived from the fast and the slow parameters in Eq. (1) is given by

$$\langle\tau\rangle = \tau_1\cdot\frac{N_1\tau_1}{N_1\tau_1 + N_2\tau_2} + \tau_2\cdot\frac{N_2\tau_2}{N_1\tau_1 + N_2\tau_2}. \tag{2}$$

Later, $\langle\tau\rangle$ will be assigned with the total decay time τ_{tot} which contains the radiative τ_{rad} and nonradiative τ_{nrad} decay times.

Thus, the decay time τ_{tot} as a function of the temperature derived from the decay curves is shown in Fig. 2a. The emission decay time of PbS QD inside polymer increases from 110 ± 10 to 480 ± 15 ns for the temperatures ranging from 300 to 4 K. Such similar quenching process of decay times at different temperatures was previously observed for dried PbS QDs with the same diameter on a glass slide, e.g. 58.9 ± 3.7 and 657 ± 10 ns for temperatures of 293 and 40 K, respectively [15]. The relatively much-longer decay times were observed for the much-smaller-diameter PbS QDs [2,17]. We also note that the decay time at

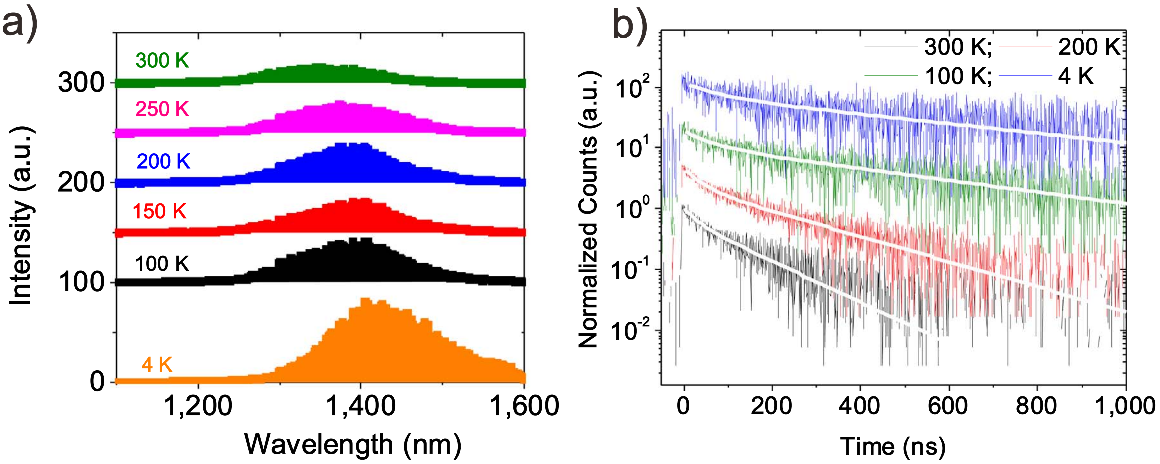

Fig. 1. (a) Photoluminescence (PL) spectra of PbS quantum dots (QDs) inside polymer matrix excited with 980-nm laser diode (LD) continuous wave (CW) laser and measured at different temperatures. (b) Temperature-dependent time-resolved PL curves of PbS QD inside polymer matrix excited with 640-nm pulsed LD laser filtered at 1400 ± 50 nm. The fits from Eq. (1) are shown by the solid white lines.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).