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Title: Enhancement of spontaneous emission of semiconductor quantum dots inside one-dimensional porous silicon photonic crystals.

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Enhancement of spontaneous emission of semiconductor quantum dots inside one-dimensional porous silicon photonic crystals: supplemental document

1 Sample synthesis and preparation

1.1 Fabrication of one-dimensional porous silicon photonic crystals

Fabrication of porous silicon (pSi) photonic crystals (PhCs) was performed using the well-known procedure of electro-chemical etching of monocrystalline p-type silicon [S1]. Etching was performed by means of a self-made etching set-up (Fig. S1) using a Si wafer with the (100) crystal orientation as the PhC substrate. The mixture of hydrofluoric acid and ethanol (v/v ratio, 3:7) was used as an etching solution. pSi layers with different porosities, which determine the optical length of the layer, were fabricated by controlling the current density (5-50 mA/cm²) and etching time. A specific order of layers with these parameters allowed us to obtain a quarter-wave stack for a selected wavelength. In this study we have fabricated two types of one-dimensional PhCs: distributed Bragg reflectors (DBRs) and microcavities. DBRs were formed by stacking 25 pairs of layers with high (75%) and low (58%) porosities, as it was estimated using the gravimetric method [S1]. pSi microcavities were formed by stacking the front and rear DBRs and the λ/2 cavity layer which was placed between them. The front and rear DBRs included 5 and 20 pairs of 75 and 58% porous layers, respectively, corresponding to the mesoporous silicon. Note that such type of porous silicon does not demonstrate inherent photoluminescent properties. The porosities and thickness of the individual layers comprising PhCs were equal for both microcavities and DBRs.

Fig. S1. The etching set-up (left) used for fabrication of porous silicon photonic crystals (right). The etched volume is shown in red.

Oxidation and silanization of porous silicon photonic crystals. After etching, PhC samples were thermally oxidized in a tube furnace (Nabertherm B180) in ambient atmosphere at 700°C for 3 h. The heating and cooling rates were maintained at 5 K/min to minimize the thermal stress in the porous structure [S2]. Scanning electron microscopy revealed that most of the pSi structure was transformed into amorphous SiO₂ without damaging the pores (Fig. S2).
The average pore diameter of the oxidized pSi decreased due to the lower molar density of SiO$_2$. However, it was still larger than the diameter of QDs; thus, oxidation did not affect the infiltration of QDs into the pores from the solution.

The reflectance spectra of porous silicon structures were shifted to the blue spectral region after oxidation due to the change in the refractive index of the quarter-wave stacks. This process allowed us to stabilize the optical properties of PhC and suppress PL quenching of the luminophores which are in direct contact with the porous surface. The value of spectral shift was used to estimate the degree of silicon oxidation by calculating the corresponding effective refractive index using the approach described in Section 3. Thus, according to our estimation, only 10% of the initial silicon in the porous structure remained intact after 3 h of oxidation at 700°C.

Finally, oxidized pSi PhCs were treated with hexadecyltrimethoxysilane (HDTMS) in order to make their surface hydrophobic and improve the infiltration of QDs. This treatment was performed by placing the PhC samples into a solution of 50 µl HDTMS in 10 ml of ethanol for 24 h, and subsequent triple washing of the samples in pure ethanol. The reflectance spectra of the PhC did not change after silanization.

### 1.2 Synthesis and embedding of CdSe (core)/ZnS/CdS/ZnS (multishell) quantum dots

CdSe(core)/ZnS/CdS/ZnS(multishell) semiconductor QDs were fabricated using the hot injection method for the synthesis of CdSe cores and an adapted SILAR procedure for subsequent shell deposition, as described elsewhere [S3]. Briefly, CdSe cores ~3.5 nm in diameter were grown in 1-octadecene (ODE) using cadmium hexadecylphosphonate and TOPSe as precursors for Cd and Se, respectively. After the isolation and intermediate purification of the cores, shell growth was performed to finally yield a complex 3-monolayer-thick ZnS/CdS/ZnS multishell. After the synthesis, the QD surface was treated with hexadecylammmonium palmitate as a surface ligand.

QDs were introduced into the pSi PhCs by drop-casting of hexane solution with a QD concentration of about 0.5 mg/ml. Deposition of small amounts (5 µl) of this QD solution onto the HDTMS-treated hydrophobic surface of oxidized pSi with a proper morphology led to uniform distribution of QDs inside the whole volume of the PhC structure, as was described earlier [S4]. Uniform distribution of QDs inside the PhC was controlled using confocal microscopy by measuring the fluorescent signal intensity along the cross-section of the PhC with embedded QDs [S4].
2 Optical characterization: reflectance, photoluminescence, and time-resolved measurements

The reflection and luminescence spectra of the fabricated samples were measured using a setup based on an Ocean Optics USB2000+ spectrometer. To measure the reflection spectra, we used a fiber reflection probe and an LS-1 broadband light source (Ocean Optics).

To excite luminescence in steady-state spectroscopy measurements, a laser diode with a wavelength of 450 nm was used. A wide-aperture achromatic optical condenser with an optic fiber port was used to collect the PL signal from the samples. The optical condenser was rotating around the sample to measure the angular distribution of luminescence. For time-resolved fluorescence spectroscopy, we used an experimental setup based on a picosecond DPSS laser with a wavelength of 532 nm and pulse duration of 350 ps, a high-resolution monochromator, and a fast PMT detector. The PL decay was measured at the wavelength corresponding to the maximum of the PL spectrum (Fig. S3).

![Experimental (symbols) and fitted (curves) PL decay of the QDs embedded in the porous silicon microcavity (red) and in the monolayer (black).](image)

Both curves could be well approximated with a biexponential function. The total relaxation time of QD PL in the microcavity was calculated using amplitude weighting [S5].

3 Calculations

3.1 Purcell effect in steady-state photoluminescence enhancement

In order to describe the optical excitation and relaxation processes in QDs, we used three-level approximation of energy states (Fig. S4) and the corresponding system of kinetic equations (S1 – S3).

![Three-level diagram. 1>, the main energy state; 2>, the excited energy state of an exciton after absorbing one photon, 3>, the energy state of the exciton after fast vibrational relaxation from state 2>.](image)
\[
\frac{dn_1}{dt} = \frac{\sigma I_{\text{ex}1}}{\hbar \omega} n_1 + \frac{\sigma I_{\text{ex}2}}{\hbar \omega} n_2 + \frac{n_1}{\tau}, \quad (S1)
\]
\[
\frac{dn_2}{dt} = \frac{\sigma I_{\text{ex}1}}{\hbar \omega} n_1 - \frac{\sigma I_{\text{ex}2}}{\hbar \omega} n_2 - \frac{n_2}{\tau_{23}}, \quad (S2)
\]
\[
\frac{dn_3}{dt} = \frac{n_2}{\tau_{23}} - \frac{n_3}{\tau}, \quad (S3)
\]
where \(n_{1,2,3}\) are populations of levels 1\(^{\text{>}}\), 2\(^{\text{>}}\), and 3\(^{\text{>}}\), respectively, \(\sigma\) is the absorption cross-section, \(\hbar \omega\) is the energy of exciting photon, \(I_{\text{ex}}\) is the pump intensity, \(\tau_{23}\) is the reversed rate of relaxation from level 3\(^{\text{>}}\) to 2\(^{\text{>}}\), and \(\tau\) is the lifetime of the 2\(^{\text{>}}\) state.

Since the relaxation rate from the 3\(^{\text{>}}\) level is several orders of magnitude higher than those of other processes in the steady state, the population of the 2\(^{\text{>}}\) level is much smaller than the populations of levels 1\(^{\text{>}}\) and 3\(^{\text{>}}\). Additionally, fast relaxation from 2\(^{\text{>}}\) to 3\(^{\text{>}}\) allows us to not consider the relaxation from level 2\(^{\text{>}}\) to level 1\(^{\text{>}}\). Thus, from equation S1, we can derive the well-known equation for population of level 3\(^{\text{>}}\):
\[
n_3 = N \cdot \frac{I_{\text{ex}}}{I_{\text{sat}}} \cdot \left(1 - e^{-\frac{t}{\tau}}\right), \quad (S4)
\]
where \(N\) is the overall concentration of QDs, \(I_{\text{sat}} = \frac{\hbar \omega}{\sigma \tau}\) is the saturation intensity. In this case, the power of the photoluminescent signal \(P\) is proportional to the product of the population of level 3\(^{\text{>}}\) and the rate of radiative emission \(\frac{1}{\tau_{\text{em}}}\):
\[
P \propto \frac{n_3}{\tau_{\text{em}}}. \quad (S5)
\]
In this study the intensity of the excitation was lower than 10 W/cm\(^2\), which is many orders of magnitude lower than the saturation intensity \((I_{\text{ex}} \ll I_{\text{sat}})\):
\[
P \propto \frac{1}{\tau_{\text{em}}} \cdot \frac{I_{\text{ex}}}{I_{\text{sat}}} \propto \frac{\tau_{\text{em}}}{\tau_{\text{sat}}}. \quad (S6)
\]
The Purcell effect in microcavities leads to an increase in the radiative emission rate and decrease in the excited state lifetime. As a result, the emission power \((P)\) grows. The rate of this growth is inversely proportional to the quantum yield of fluorescence \((QY)\). In the case of \(QY = 1\) \((\tau = \tau_{\text{em}})\), the Purcell effect does not affect the emission power. Below we write the equation for the factor of intensity enhancement due to the Purcell effect \((f = P_{\text{cav}} / P_0)\) as a function of parameters that could be measured experimentally: \(QY\); the quantum yield of the emission of QDs inside the porous monolayer; \(\tau_0\); excited state lifetime of QDs inside the porous monolayer; \(\tau_{\text{cav}}\); the excited state lifetime of QDs inside the porous silicon microcavity.
\[
f = \frac{P_{\text{cav}}}{P_0} = \frac{\tau_{\text{cav}}}{\tau_0} \cdot \frac{\tau_{\text{em}}}{\tau_{\text{em}}} \cdot \frac{\tau_0}{\tau_0} \cdot \frac{\eta}{\tau_0}, \quad (S7)
\]
where \(\eta\) is the Purcell factor.
\[
\frac{1}{\tau_0} = \frac{1}{\tau_{\text{em}}} + \frac{1}{\tau_{\text{cav}}}; \quad \frac{1}{\tau_{\text{cav}}} = \frac{\eta}{\tau_{\text{em}}} + \frac{1}{\tau_0}; \quad QY = \frac{\tau_0}{\tau_{\text{em}} + \tau_{\text{cav}}}. \quad (S8)
\]
Using simple transformations, we obtain the equation for the Purcell factor as a function of \(\tau_0\), \(\tau_{\text{cav}}\), and \(QY\):
\[
\eta = 1 + \left(\frac{\tau_0}{\tau_{\text{cav}}} - 1\right) \cdot \frac{1}{QY}. \quad (S9)
\]
Finally, from (S7) and (S9), we obtain:
\[
f = \frac{\tau_{\text{cav}}}{\tau_0} + \left(1 - \frac{\tau_{\text{cav}}}{\tau_0}\right) \cdot \frac{1}{QY}. \quad (S10)
\]
Substituting the experimental values obtained from the kinetic measurements, we can estimate the intensity enhancement factor \( f \) to be around 1.7.

### 3.2 Calculations of the photonic crystal optical properties, density of photonic states, and emission alteration

The optical properties of the PhC were calculated using the transfer matrix method [S6]. In accordance with the experimental parameters of the sample, the Bragg mirror consists of 25 pairs of periodically alternating layers with widths of 78 nm and 105 nm and initial porosities of around 58% and 75%, respectively. The refractive indices of these layers depend on the porosity index, which was calculated in two steps. At the first step, the refractive index of the solid structure consisting of Si and SiO\(_2\) was computed using the Bruggemann model of effective medium [S7]. At the second step, the influence of the sample oxidation on the porosity was taken into account, as it had been performed elsewhere [S7]. The recalculated porosity index was used for computing the refractive index of the porous layers in the PhC via the two-component effective medium model. The dispersion and wavelength-dependent absorbance of Si and SiO\(_2\) were also taken into account [S8]. The calculated transmission spectra of the samples were used for computing the spectral distribution of the photonic density of states and PL spectra of QDs embedded inside the pSi DBR [S9]. For precise calculation of the angular dependences of the enhanced PL spectra, the configuration of the experimental set-up was taken into consideration. The condenser lens collected the emission radiated into a finite solid angle. In order to take this fact into account, we computed the whole intensity captured by the condenser lens (Fig. S5).

![Fig. S5. Detection of the luminescence intensity of the sample. The grey area represents the part of emission that is captured by the condenser lens and therefore contributes to the signal. \( \theta_c \) is the angle between the normal vector of the sample surface and the vector from the sample surface center to the lens center.](image)

The full PL signal collected by the detection system can be calculated from the equation:

\[
I(\lambda, \theta) = \frac{\int_{\Omega_{\text{in}}(\theta_c)} I_0(\lambda, \theta) dS}{\int_{\Omega_{\text{in}}(\theta_c)} dS},
\]

where \( \Omega_{\text{in}}(\theta_c) \) is the lens surface, \( \theta = \arccos \frac{z}{\sqrt{x^2 + y^2 + z^2}} \), \( I_0(\lambda, \theta) \) is the luminescence intensity of the sample. The latter can be represented in the following way:

\[
I_0(\lambda, \theta) = C I_{\text{fs}}(\lambda) \cos \theta \cdot \rho(\lambda, \theta),
\]

where \( I_{fs}(\lambda) \) is the QD spectrum in free space, \( \rho(\lambda, \theta) \) is the photonic density of states induced by the PhC relative to the one in the free space, \( C \) is the proportionality constant independent of \( \lambda \) and \( \theta \). This function also includes the cosine multiplier which corresponds to the angular pattern of radiation emitted by the flat surface source into free space in accordance with the Lambert law. Changing to the coordinate system rotating by the angle \( \theta_c \) on the axis \( Y \) (\( X'Y'Z' \))...
with respect to the reference one (XYZ), we derive the final equation for the light intensity captured by the detector:

\[ I(\lambda, \theta') = \frac{1}{\pi r^2} \int_{-r}^{r} \int_{-\sqrt{r^2-x^2}}^{\sqrt{r^2-x^2}} I_0(\lambda, \theta(x', y')) \, dy', \]  

(S13)

where \( r \) is the lens radius, \( \theta(x', y') = \frac{z' \cos \theta - x' \sin \theta}{\sqrt{x'^2 + y'^2 + z'^2}} \), \( z' \) is fixed in this coordinate system and is equal to the distance between centers of the lens and of the sample surface. The obtained integral was calculated numerically using the Monte Carlo method.

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