Enhancement of the photoluminescence of semiconductor nanocrystals in transfer-printed microcavities based on freestanding porous silicon photonic crystals

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Abstract. Today, lots of research address the phenomenon of interaction between light and matter. In particular, it is of a special interest to investigate light–matter interaction in one-dimensional resonators based on porous materials. In this case, one can embed emitting semiconductor particles into the porous resonator, where the excitons of these particles couple to the resonator eigenmode and luminescence intensity of the emitters is enhanced, allowing an increase in the sensitivity of optical sensors, detectors, and photonic diagnostic assays. A particular challenge is to place the emitters directly in the antinode region of the resonator eigenmode in order to maximize the coupling strength, which is sometimes a problem due to the spatial distribution of emitters away from the eigenmode localization region. Here, we have shown that the transfer-printing technique can be used to obtain structures based on freestanding porous silicon photonic crystals capable of precisely controlling the emitter spatial distribution about the eigenmode localization region. This, as well as the porosity of these structures and high adsorption capacity of porous silicon, allows the light–matter interaction in these hybrid structures to be used in sensing applications. We have shown that the transfer-printing method does not worsen the optical properties of the microcavities compared to the conventional electrochemical etching of the whole microcavity at a time. Furthermore, we have observed slightly better coupling of the exciton of the emitter to the eigenmode of the transfer-printed microcavity in the weak coupling regime.

1. Introduction

At present, light–matter interaction of excited states of an emitter in a cavity and the localized electromagnetic field is of a great interest for fundamental research as well as practical applications, in particular, sensing. Their interaction could cause coherent energy transfer between the cavity mode and the emitter [1]. The properties of the coupled system depend on the decay rates of the cavity and emitter and the rate of coherent energy exchange in the system, i.e., the coupling strength. The ratio of these rates determines whether the interaction regime will be weak or strong [2]. In the case of strong coupling, when the rate of coherent energy exchange between the emitter and cavity exceeds their decay rates, two new hybrid eigenstates are formed instead of previous ones. This effect could be observed in reflection, transmission, or even luminescence spectra [1,3] as Rabi splitting of the specific eigenenergy

peak into two separate peaks. In this study, the weak coupling regime is considered, which occurs if the decay rates prevail over the coupling strength. In this case, the Purcell effect is observed, i.e., the enhancement of the spontaneous emission rate due to the modification of the photon density of states. For both cases, most of the light–matter interaction applications are based on one-dimensional resonators, which can be based, in particular, on one-dimensional photonic crystals. At the same time, porous structures are of particular interest in this research area. Embedment of organic or inorganic luminophores (such as semiconductor nanocrystals, also known as quantum dots (QDs), polymers, or dyes) into such structures makes it possible to control light emission, which is required in various applications, e.g., lasers [4] and displays [5]. This also has implications for fundamental investigations of the effects related to light–matter interaction [1]. One of the most convenient and well-studied materials for one-dimensional photonic crystals is porous silicon (PSi). Microcavities with a relatively high Q-factor can be fabricated on the basis of PSi in a wide wavelength range [6] due to the possibility to precisely control the porosity during the electrochemical anodization, simply by varying the etching parameters [7]. In the case of embedding luminophores into porous microcavities, the light–matter interaction efficiency is directly proportional to the intensity of the electric field component near the luminophore [1], and the electromagnetic field in the microcavity is mostly localized in the region of eigenmode localization. Therefore, it is required to develop a technique for manufacturing porous microcavities with luminophores placed precisely in the eigenmode localization area to explore new possible applications of light–matter interaction.

2. Materials and methods

The technology of manufacturing transfer-printed PSi microcavities used in this study is based on the electrochemical etching of monocrystalline silicon and detaching PSi structures from the monocrystalline substrate by electropolishing in a water–alcohol solution of hydrofluoric acid (HF). For detaching the porous layers from the substrate, the electropolishing regime requires a much higher etching current density compared to the PSi formation regime (up to 300 mA/cm^2, using a 15% water–alcohol solution of HF as an electrolyte). However, it has been shown that a diluted solution of HF can improve the surface quality of the obtained porous structures [8]. In a fluorine-depleted solution, an electrochemical anodizing process leads to the formation of oxygen compounds of silicon at the PSi/monocrystalline substrate interface, where the holes provided by the substrate are readily available to promote the silicon oxidation. Subsequent interaction with fluorine ions leads to the dissolution of the oxide layer, resulting in the separation of the PSi structure from the substrate. In addition, a lower concentration of HF makes it possible to reduce the etching current density necessary for detaching by one or two orders of magnitude [9]. Therefore, an etching current density of less than 5 mA/cm^2 was used here for the detaching PSi structure from the Si substrate in a 1.6% water–alcohol solution of HF.

The process of transfer-printed PSi microcavity fabrication is shown schematically in Figure 1a. The bottom Bragg mirror, also referred to as a distributed Bragg reflector (DBR), was fabricated together with a cavity, as a defect layer of double thickness for creating a microcavity eigenmode, on a monocrystalline silicon substrate; the top DBR was fabricated separately, detached from its substrate (Figure 1b) and placed above the bottom DBR. To obtain a hybrid structure, we used CdSe/CdS/ZnS QDs as the emitter because they have the specific advantages of a wide absorption and a narrow luminescence spectra, high quantum yield, and high photostability. The absorption and luminescence spectra of the QDs solution in hexane used here can be seen in Figure 2. Their mean diameter was measured by a JEOL JEM-2100F TEM and found to be about 6.5 nm, and their photoluminescence emission peaks at 606 nm. Since we had an access to the cavity region during the hybrid system fabrication, a highly concentrated solution of the QDs was used to embed them exactly into the cavity prior to covering it with the top DBR, by QD solution drop casting (Figure 1a).

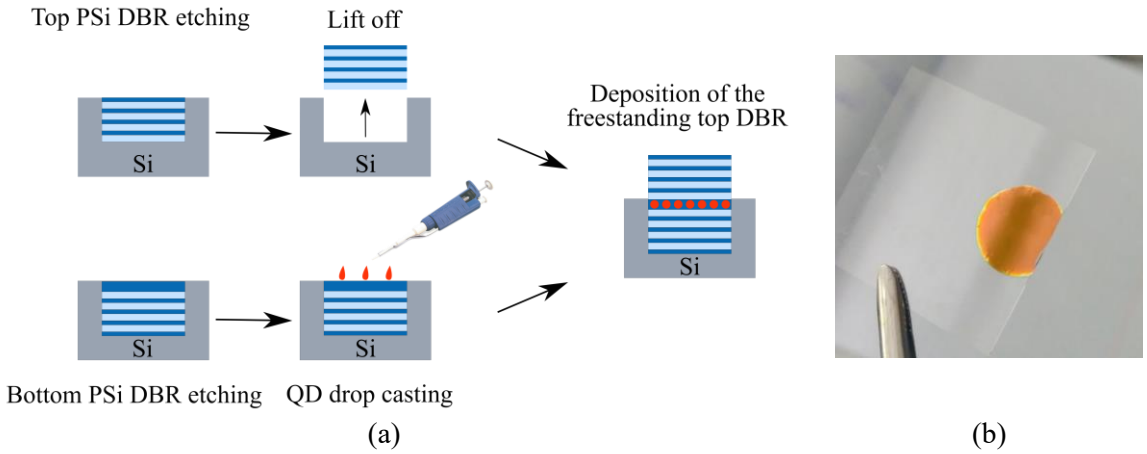

Figure 1. (a) Schematic illustration of the transfer-printed microcavity fabrication and (b) a micrograph of freestanding top PSi DBR lifted off from the Si substrate.

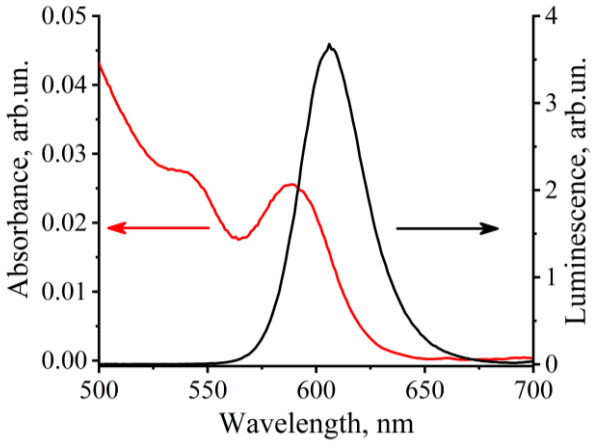

Figure 2. The absorption (red) and luminescence (black) spectra of the CdSe/CdS/ZnS QD solution.

The reflection spectra were measured using an Ocean Optics USB2000+ spectrometer and an LS-1 Tungsten Halogen Lamp as a source. In luminescence measurements, the same spectrometer was used with a 440 nm CW excitation laser.

3. Results and discussion

In order to control the influence of transfer-printing on the optical properties of the microcavity, we have fabricated the microcavity with the same morphology using conventional electrochemical etching of the whole microcavity at a time. The results of reflectivity measurements for both types of the microcavities are shown in Figure 3. The full-width-at-half-maximum of the photonic band gap and the eigenmode were about 150 nm and 5 nm, respectively, for both conventional "one-piece" (Figure 3a) and transfer-printed (Figure 3b) microcavities. The Q-factor was found to be about 130, which is a typical value for PSi microcavities in this wavelength range of the optical spectrum [9,10]. The high coincidence between the optical characteristics of the "one-piece" and transfer-printed microcavities indicates that the presented technique of manufacturing transfer-printed microcavities does not affect their optical properties, namely, the reflectance (over 99%) and a relatively high Q-factor, because the morphology of porous structure did not change during the transfer-printing process.

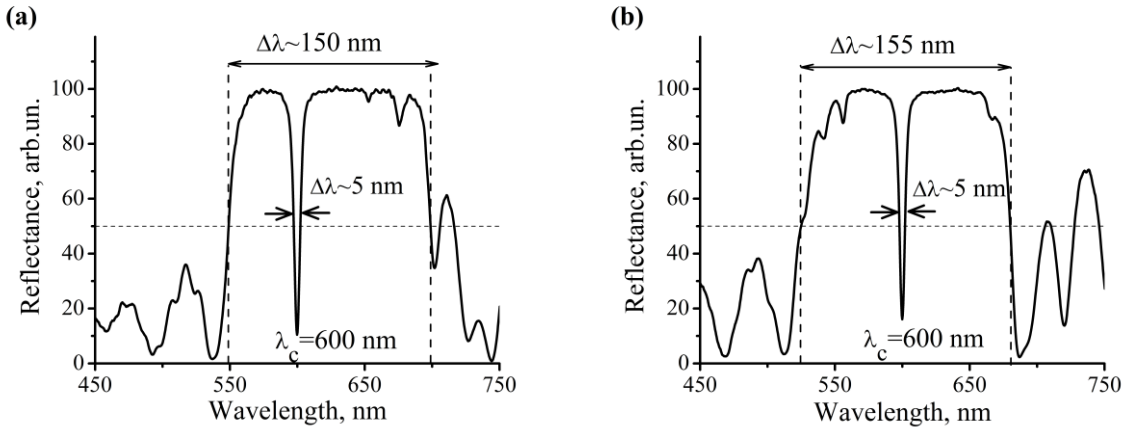

Figure 3. Reflectance spectra of (a) a conventional "one-piece" and (b) a transfer-printed PSi microcavities.

When the emitting particles are placed in a microcavity, their luminescence spectrum undergoes some changes depending on the conditions of the experiment, such as the microcavity Q-factor, its mode volume, and, hence, the coupling strength between the exciton in the emitter and the microcavity eigenmode. Given the relatively large mode volume and low microcavity Q-factor, the Purcell effect takes place, which is an increase in the spontaneous emission rate and luminescence intensity of the emitter in the cavity at its eigenmode wavelength compared to the free-space [11]. This effect strongly depends on the emitter distribution in the microcavity (in our case, in a PSi photonic crystal). It has been shown [12] that excitons in QDs remote from eigenmode localization region are less coupled to the microcavity eigenmode, in which case, the Purcell effect is sometimes absent at all.

Here, QDs were embedded into a conventional "one-piece" microcavity by drop casting of a QD solution onto the top DBR, whereupon QDs diffused into the structure pores and distributed in the top DBR and in the microcavity eigenmode localization region. In the case of the transfer-printed microcavity, QDs were placed directly into the eigenmode localization region. In the conventional "one-piece" microcavity, the full-width-at-half-maximum of the QD luminescence spectrum narrowed from 35 nm for the QD solution to 10 nm (Figure 4). In the transfer-printed microcavity, we observed a slightly better result: the luminescence spectrum of QDs in the eigenmode localization region narrowed to 9 nm. We believe that the difference in the narrowing of the QD luminescence spectra is caused by a more efficient coupling of excitons of QDs to the eigenmode of the transfer-printed microcavity compared to the "one-piece" microcavity, due to the more appropriate spatial distribution of QDs about the eigenmode localization region. Thus, the optical properties and luminescence-enhancing efficiency of both types of microcavities seem to be nearly the same. At the same time, the transfer-printed microcavity has the advantage of the possibility of placing luminophores exactly into its eigenmode localization region, and we assume that this will allow us to increase the coupling strength and achieve the strong coupling regime of light–matter interaction.

Indeed, the resulting narrowing of the luminescence spectra is observed due to the enhancement of QD luminescence at the microcavity eigenmode wavelength and its suppression at the other wavelengths in the photonic band gap. The Purcell effect is also known to be a straightforward indication of weak coupling between the microcavity eigenmode and the QD exciton [13]. In this case, the coherent energy exchange rate (i.e., coupling strength) is lower than the average of the inverse lifetimes of the cavity photon and exciton [14]. We expect that further increase in the electromagnetic field localization and control of the spatial distribution of the emitters in the eigenmode localization region of the transfer-printed microcavity will result in a coupling strength high enough to compensate for the losses in the hybrid system and obtain a strong coupling regime.

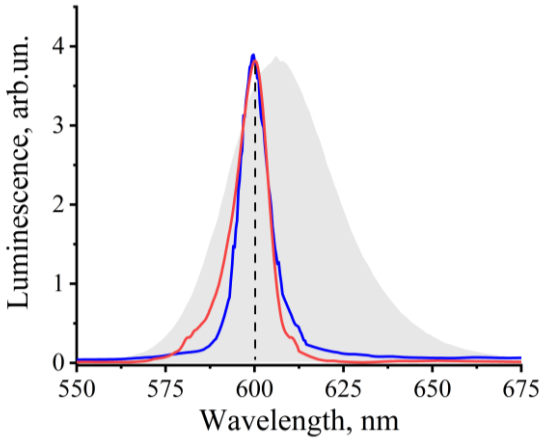

Figure 4. Luminescence spectra of QDs in a solution (gray area) and in the eigenmode localization region of a conventional "one-piece" (red curve) and a transfer-printed (blue curve) PSi microcavities. The dashed line indicates the microcavity eigenmode wavelength.

4. Conclusion

Here, we have manufactured, and compared the optical and fluorescence-enhancing properties of, hybrid systems based on PSi photonic crystal and luminophores located in the region of spatial localization of the eigenmodes of (1) transfer-printed microcavities based on a freestanding photonic crystal and (2) conventional "one-piece" microcavities formed on a monocrystalline silicon substrate. Comparison of the reflection spectra of the two types of microcavities revealed that their optical characteristics are in good correlation; therefore, the transfer-printing technique used in this study does not affect the quality of the microcavities or the morphology of their porous structure. Analysis of QD luminescence spectra demonstrates a threefold decrease in its full-width-at-half-maximum for QDs embedded into both types of microcavities compared to the QD solution spectrum, which indicates luminescence enhancement due to the Purcell effect in the cavity and weak coupling between the QD exciton and the microcavity eigenmode. The optical and luminescence-enhancing properties of "one-piece" and transfer-printed microcavities seem to be nearly identical; however, transfer-printed microcavities allow luminophores to be placed directly into the microcavity eigenmode antinode region in order to increase the strength of coupling between the eigenmode and the exciton in the luminophore. The technique of manufacturing microcavities with emitting particles located exactly in the eigenmode localization region developed here lays the foundation for investigating new breakthrough effects associated with the light–matter interaction and reveals new prospects for studying light emission control and associated applications. Moreover, of particular interest for sensing applications are studies on media with different refractive indices adsorbed by these hybrid structures and their effects on the optical properties of the hybrid system and the strength of coupling between its components.

Acknowledgments

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References

[1] Dovzhenko D S, Ryabchuk S V., Rakovich Y P and Nabiev I R Light–matter interaction in the strong coupling regime: configurations, conditions, and applications 2018 *Nanoscale* **10** 3589–605

[2] Khitrova G, Gibbs H M, Kira M, Koch S W and Scherer A Vacuum Rabi splitting in semiconductors 2006 *Nat. Phys.* **2** 81–90

[3] Dovzhenko D, Mochalov K, Vaskan I, Kryukova I, Rakovich Y and Nabiev I Polariton-assisted splitting of broadband emission spectra of strongly coupled organic dye excitons in tunable

optical microcavity 2019 *Opt. Express* **27** 4077
[4] Reece P J, Gal M, Tan H H and Jagadish C Optical properties of erbium-implanted porous silicon microcavities 2004 *Appl. Phys. Lett.* **85** 3363–5
[5] Schubert E F Solid-State Light Sources Getting Smart 2005 *Science* **308** 1274–8
[6] Kotkovskiy G E, Kuzishchin Y A, Martynov, I L, Chistyakov A A and Nabiev I The photophysics of porous silicon: technological and biomedical implications 2012 *Phys. Chem. Chem. Phys.* **14** 13890-902
[7] Smith R L and Collins S D Porous silicon formation mechanisms 1992 *J. Appl. Phys.* **71** R1–22
[8] von Behren J, Tsybeskov L and Fauchet P M Preparation and characterization of ultrathin porous silicon films 1995 *Appl. Phys. Lett.* **66** 1662–4
[9] Sailor M J Freestanding Porous Silicon Films and Particles 2012 *Porous Silicon in Practice* (Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA) pp 119–31
[10] Dovzhenko D S, Martynov I L, Kryukova I S, Chistyakov A A and Nabiev I Modeling of the optical properties of porous silicon photonic crystals in the visible spectral range 2017 *Optics and Spectroscopy* **122** 79–82
[11] Purcell E M Spontaneous emission probabilities at radio frequencies 1946 *Phys. Rev.* **69** 681
[12] Dovzhenko D S, Martynov I L, Samokhvalov P S, Mochalov K E, Chistyakov A A and Nabiev I Modulation of quantum dot photoluminescence in porous silicon photonic crystals as a function of the depth of their penetration 2016 *Proc. SPIE* **9885** 988507
[13] Noda S, Fujita M and Asano T Spontaneous-emission control by photonic crystals and nanocavities 2007 *Nat. Photonics* **1** 449–58
[14] Solomon G S, Pelton M and Yamamoto Y Single-mode spontaneous emission from a single quantum dot in a three-dimensional microcavity 2001 *Phys. Rev. Lett.* **86** 3903–6