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## Spontaneous emission control of colloidal nanocrystals using nanoimprinted photonic crystals

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The authors report on the fabrication and optical characterizations of two-dimensional photonic crystals fabricated by nanoimprint lithography in a nanocomposite polymer incorporating highly luminescent and red emitting (CdSe)ZnS core-shell colloidal nanocrystals. Photonic crystal structures enhance the light emitted from the quantum sized nanoparticles in the composite layer by slowing the propagation speed of the photons, thus increasing the coupling to the out-of-plane radiative modes. A 200% enhancement of the light collection is achieved compared to an unpatterned sample. © 2007 American Institute of Physics. [DOI: 10.1063/1.2430625]

In the last years, inorganic nanocrystals (NCs) exhibiting quantum confinement regime have generated interest as efficient luminophores, due to their narrow and intense optical emission which can be tuned across the visible spectrum by simply modifying the particle size. These properties have opened a number of potential applications. For example, light-emitting diodes (LEDs) based on colloidal nanocrystals embedded in conjugated polymers with emission from visible up to infrared region of the spectra range have been demonstrated.<sup>1,2</sup> One of the critical issues for optoelectronic emission devices, is the improvement of the external efficiency of organic LEDs, because an important part of the photons is trapped by total internal reflection in the active layer. Several techniques have been reported to achieve higher efficiency by modifying the spontaneous emission characteristics or the LED geometry. For example, random surface texturing such as nanoporous alumina film,<sup>3</sup> microcavities,<sup>4</sup> plasmon surface,<sup>5</sup> and bidimensional photonic crystals<sup>6-8</sup> (PhCs) have been tested. One approach is the use of photonic crystals, which are periodic dielectric structures with a periodicity in the order of the wavelength of light to give a particular dispersion to photons. Functional optical devices are expected by using PhCs, as ultracompact bent waveguides, superprism phenomenon,<sup>9,10</sup> self-collimated beam propagation,<sup>11,12</sup> and add-drop filter<sup>13</sup> among them. PhC structures are usually produced by electron-beam lithography and dry-etching methods such as reactive ion etching techniques. In order to replace these expensive and time-consuming techniques, nanoimprint lithography has been recently proposed as a high volume and cost-effective patterning technique with sub-10 nm resolution.<sup>14</sup> Nanoimprint lithography (NIL) and its related techniques have demonstrated especially its capacity to fabricate organic

photonic devices. For example, polymer waveguide-type wavelength filter based on a Bragg grating,<sup>15</sup> microring resonator,<sup>16</sup> lasers,<sup>17</sup> and photonic crystals<sup>18,19</sup> has been recently demonstrated by NIL.

In this letter, we report on the optical characterization of photonic crystal structures nanoimprinted in a photoluminescent nanocomposite material based on a polymer resist and highly luminescent semiconductor nanocrystals. Red emitting (CdSe)ZnS core-shell quantum dots have been synthesized by thermal decomposition of precursors in organic surfactants<sup>20</sup> and incorporated in a printable polymer (mr-NIL 6000 from micro resist technology), which is optically transparent in the visible range. The optical properties of the photonic crystals fabricated by NIL have been measured and compared to those of the unpatterned samples. No evidence of degradation of the light-emitting materials after patterning is found. A photoluminescence (PL) enhancement by a factor of 2.2 is achieved using a two-dimensional (2D) honeycomb lattice of air hole PhCs. This PL enhancement is close to the enhancement observed in inorganic devices<sup>21,22</sup> and well above that measured in organic devices.<sup>23,24</sup>

In order to investigate the effect of the embedding in polymer on the NC optical properties, absorption and emission spectroscopies were performed using standard equipment. In Fig. 1, the absorption (ABS) and the luminescence spectra (PL) of the nanocrystals in their native solution and after incorporation in mr-NIL 6000 are shown. The absorption spectra show a main peak due to the first allowed optical transition in NCs. The comparison between the ABS spectra confirms that the embedding in polymer does not modify the optical properties of the NCs. The PL spectra are dominated by a strong and narrow, excitation independent, band edge emission in the red region with a full width at half maximum of about 38 nm, indicating a narrow particle size distribution. In addition, a doubling in the emission quantum yield was

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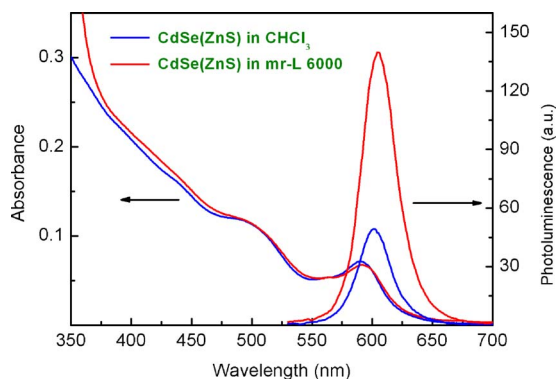


FIG. 1. (Color online) Comparison between absorption and PL spectra of (CdSe)ZnS NCs in their native solution (blue line) and after the incorporation in the mr-NIL 6000 polymer (red line) at room temperature (excitation wavelength of 400 nm).

measured (data not reported), which can be reasonably ascribed to a better passivation of NC surface<sup>25</sup> when embedded in the polymer. The polymer mr-NIL 6000, after (CdSe)ZnS NCs incorporation, is spin coated on fused silica substrate at a speed of 1000 rpm for 1 min and soft baked at 120 °C for 5 min to evaporate the residual solvent.

Nanoimprint experiments were carried out in a 2.5 in Obducat nanoimprinting equipment. Silicon stamps with two-dimensional photonic crystals were fabricated by electron-beam lithography using a conventional silicon process and treated with an antiadhesive layer (tridecafluor-1,1,2,2-tetrahydrooctyl trichlorosilane) deposited in vapor phase, which results in a very low surface energy to avoid adhesion between the polymer and the stamp during demolding. The silicon was etched with a depth of 350 nm by dry etching [Fig. 2(a)]. Then, the stamp is pressed onto the substrate at a temperature of 100 °C and under a pressure of 60 bars for 500 s. The pressure is sustained until the temperature falls below 35 °C and the mold and substrate are then separated. Figure 2(a) presents a tilted view of the silicon stamp and Fig. 2(b) shows nanoimprinted photonic crystals in the nanocomposite thin film.

The nanoimprinted samples on fused silica substrates are optically excited using the emission of a continuous wave Ar<sup>+</sup> laser at a wavelength of 514.5 nm, with a power of 240  $\mu$ W focused down to a 10  $\mu$ m spot with the incident beam normal to the surface. The excitation light is absorbed by the polymer/(CdSe)ZnS NC nanocomposite and the PL collection cone is defined by a 10 $\times$  microscope objective with a numerical aperture NA=0.4. PL coming from the fused silica substrate is negligible. PL spectra from the collection spot on the sample were measured normal to the surface and analyzed with an optical spectrum analyzer on a 530–750 nm with a resolution of 0.1 nm.

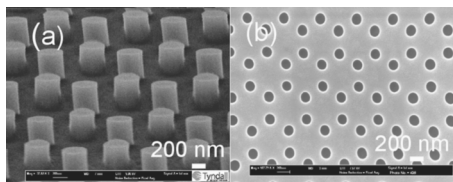


FIG. 2. (Color online) (a) Scanning electron microscopy (SEM) micrographs of tilted view of a silicon stamp containing two-dimensional honeycomb array of pillars. (b) SEM micrographs of nanoimprinted photonic crystals in mr-NIL 6000 containing (CdSe)ZnS NCs.

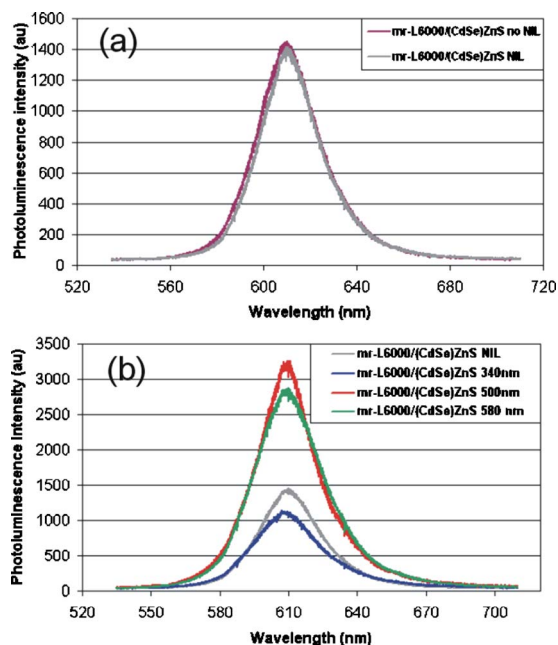


FIG. 3. (Color online) (a) Emission spectra for (CdSe)ZnS NCs taken before (violet solid line) and after (gray solid line) the nanoimprint process. (b) PL spectra of nanoimprinted unpatterned mr-NIL 6000 with (CdSe)ZnS NCs on a Pyrex substrate (gray line), PL spectra of a 2D photonic crystal with a 340 nm lattice constant and hole radius of 112 nm (blue line), with a 500 nm lattice and hole radius of 166 nm (red line), and with a 580 nm lattice and hole radius of 192 nm (green line).

The most crucial test for the effectiveness of the whole imprinting process is the preservation of the optical properties of the NCs. This is not trivial because of the sensitivity of the NC optical properties, and especially their emission, to surface passivation, high pressure, and important temperature variation occurring during the NIL process. The comparison between the emission spectra of the mr-NIL 6000 polymer/(CdSe)ZnS NC composite thin film deposited on a fused silica substrate before and after imprinting with a flat stamp is presented in Fig. 3(a). The nanocomposite is printed at 100 °C at a pressure of 60 bars for 500 s. The emission from the thin film as deposited shows an almost identical emission from the imprinted film. This demonstrates that the nanoimprint process has a negligible impact on the optical properties of the NCs.

Using the same experimental setup, PL spectra of three PhCs with different lattice constants and with the same air-filling factor of 40% (blue line, lattice constant  $a=340$  nm; green line,  $a=580$  nm; and red line,  $a=500$  nm) are recorded and shown in Fig. 3(b). The PL intensity of the 340 nm lattice constant PhC is slightly lower compared to that of the nanoimprinted unpatterned substrate. On the other hand, while for a PhC with a lattice constant of 580 nm, an enhancement by a factor of 2.2 in the PL intensity is observed. A factor of 2 is also measured in the PL intensity of the 500 nm lattice constant sample.

The 2D band diagram, i.e., the dispersion diagram for the photons propagating in the plane of the PhC, of the honeycomb lattice calculated using a plane wave algorithm is reported in Fig. 4 for both transverse electric (TE) and transverse magnetic (TM) polarizations. The effective refractive index of a 500 nm thick mr-NIL 6000 layer on fused silica has been measured at a wavelength of 614 nm to a value of 1.578. The slight decrease of PL intensity for the 340 nm lattice constant PhC can be ascribed to its band structure. In

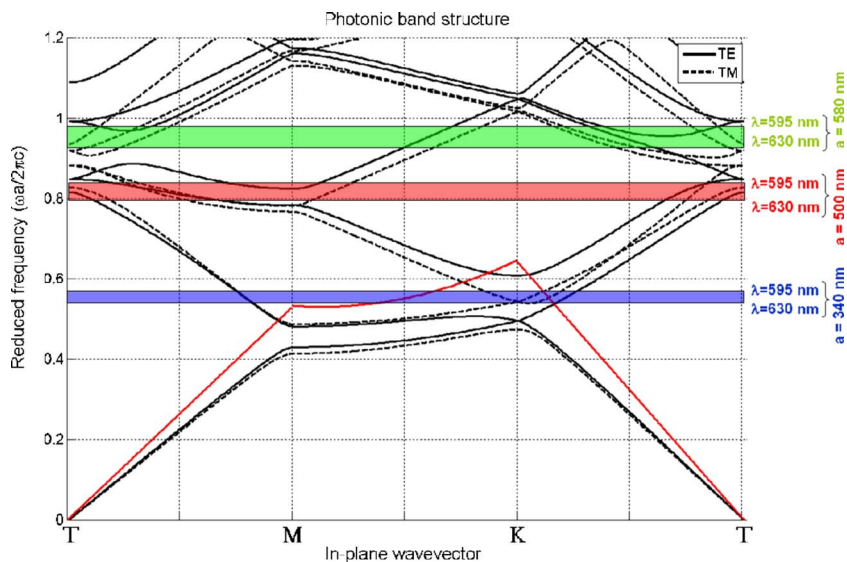


FIG. 4. (Color online) Photonic band structure of a honeycomb lattice of air hole PhC calculated with a plane-wave-basis frequency-domain method (dotted lines, TM polarization; solid lines, TE polarization)  $a$  is the lattice constant,  $\lambda$  is the wavelength, and  $c$  is the light speed in vacuum. Holes radius is  $R=0.332a$ . The blue, red, and green bands correspond to the emission bandwidth of (CdSe)ZnS for PhC lattice constants  $a=340$  nm,  $a=500$  nm, and  $a=580$  nm, respectively. The red line represents the light cone.

this case, the in-plane propagating modes corresponding to the NC emission linewidth (blue band in Fig. 4) are below the light cone, which is the limit of the strictly guided modes in the PhC slab represented by the red line in Fig. 4, and exhibit a flat dispersion. This has as consequence a large density of modes and a low group velocity. Consequently, a higher concentration of light in the guided modes in the plane, even compared to the unpatterned sample, is expected resulting in less light extracted out of the plane.

Above the light cone, modes are leaky. They act as a doorway to the free space out of the slab. Furthermore, in this frequency range, relatively “flatbands” exist near the  $\Gamma$  point of the reciprocal lattice. Therefore, as these modes display a low group velocity, photons can couple to the radiating modes after a short mean free path in the PhC slab. Moreover, the enhanced density of states is situated near the  $\Gamma$  point. Light is then mostly extracted into directions perpendicular to the PhC slab. In the configuration studied, a PL enhancement by a factor of 2.2 is observed. When the lattice constant is 500 nm, a PL enhancement of 2 is measured. The difference of PL enhancement between 500 and 580 nm lattice constants may be due to the different group velocity of photons and by this way to different density of states. A rigorous calculation of the local density of state is necessary in order to explain these differences of PL enhancements.<sup>26</sup>

In conclusion, 2D honeycomb lattices of air hole PhCs have been fabricated by nanoimprint lithography in a nanocomposite material based on mr-NIL 6000 resist with (CdSe)ZnS colloidal nanocrystals on fused silica substrates. Photoluminescence of these samples with different lattice constants have been presented. Light is efficiently extracted in specific directions near the perpendicular direction by scaling the PhC and using particular points of the PhC band structure. An enhancement of the light collection of up to 2.2 is achieved compared to a nanoimprinted unpatterned sample. These results could have applications for the fabrication of white-light-emitting diodes by a cost efficient lithography technique, namely, nanoimprint lithography.

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