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## ABSTRACT

Core/shell CdSe/CdZnS nanoplatelets (NPLs) are a promising class of nanomaterials for lasing applications owing to their low thresholds and high stability of stimulated emission generation as compared with many other types of colloids. Moreover, they can be self-assembled into high-quality thin films by simple methods of deposition. However, the high throughput and reproducible methods for nanopatterning of such films for advanced light-emitting applications are still missing. In this work, we show direct laser writing on thin films assembled from CdSe/CdZnS NPLs using either spin-coating or the self-assembly method for the purpose of fabricating. Using theoretical calculations, we design the period of the structures to achieve high quality-factor optical modes in the emission band of NPLs. In these nanostructured NPL films, fabricated according to the design, we observe photoluminescence enhancement and directional outcoupling effects. The proposed approach holds great potential for LEDs with improved outcoupling and for distributed feedback lasers or lasers based on bound states in the continuum with directly written optical cavities.



Two-dimensional semiconductor nanoplatelets (NPLs) forming colloidal quasi-two-dimensional quantum wells (QWs) are one of the most rapidly developing areas of photonic nanomaterials. Auger recombination is the main fundamental obstacle to achieving low-threshold amplified spontaneous emission (ASE) and hinders the achievement of population inversion.[1] NPLs with their quasi-2D quantum structure exhibit reduced Auger recombination rates, while delocalization of charge carriers in the plane of NPL ensures the coexistence of several excitons and reduces the probability of exciton– exciton annihilation.[2] The combination of these characteristics in NPLs makes them an excellent medium for achieving low-threshold lasing and highly efficient LEDs.[3,4]

For example, one of the highest values of a net modal gain for CdSe-core NPLs was demonstrated to be around 6600 $cm^{-1}$.[5] Such core-only NPLs may exhibit low ASE thresholds but typically lack a high quantum yield and suffer from trap states, due to the presence of dangling bonds at the surface and poor passivation solely with ligands. The solution to this problem was to coat additional layers around the core to create a core–shell structure. Such heterostructured NPLs have unique luminous characteristics and low-threshold emission amplification on par with the best light-emitting materials.[6] The best emission amplification performance reported for NPLs so far was achieved by creating alloyed hot injection CdZnS shells on top of a CdSe core.[7] The resulting NPLs showed not only a very low ASE threshold of 2.35 $\mu J/cm^2$ but also increased chemical and thermal stabilities.

These unique properties make NPLs an extremely promising platform for next-generation lasers. However, another prerequisite on route toward lasing is an optical cavity with positive optical feedback. Cavity architectures are extremely diverse and include Fabry–Perot[8] and whispering-gallery-mode resonators,[9] Mie resonators,[10] bound-states-in-the-continuum,[11] and various other planar designs. In particular, meticulously designed lithographic nanostructures supporting high quality-factor (Q-factor) optical modes can be integrated with light-emitting materials, including NPLs. Recently, a low lasing threshold of 44.5 $\mu$J/cm$^2$,[12] has been demonstrated in an array of $TiO_2$ nanocylinders supporting Mie-resonant bound-states-in-the-continuum and coated on top with a layer of CdSe/CdZnS NPLs. Also, the CdSe/CdS@$Cd_{1-x}Zn_xS$ core/crown@graded alloy shell NPLs film was created around a coreless fiber to construct a ring resonator with whispering gallery modes,[13] providing a lasing threshold around 188 $\mu$J/cm$^2$ and a net modal gain coefficient of 485 cm$^{-1}$. Multi-step lithography approach was also previously used for creating self-resonant microlasers made of colloidal NPLs,[14] where the reported lasing threshold was around 21 $\mu$J/cm$^2$. As an alternative simple but versatile technique to define possibly a wide range of optical cavities, direct laser writing (DLW) approach was successfully used for nanopatterning of light-emitting materials with relatively low thermal conductivity.[15,16] The key to the success of direct writing is preventing the overheating of the remaining material surrounding the ablated regions. In this regard, films made of NPLs separated by ligands should also possess critically reduced heat transport, which may then prove to be a promising tool for fabrication of light-emitting devices and lasers using the DLW approach.

In this work, we develop and demonstrate the DLW method for directly structuring thin films made of CdSe/CdZnS nanoplatelets using two alternative coating techniques of spin-coating and oriented self-assembly. The structuring capabilities of the DLW make it possible to create nanostructures with small and controllable periods that support optical modes in these NPL films at different wavelengths in the proximity of the emission band of the NPLs. The improved directionality and photoluminescence enhancement achieved with nanostructured NPL films created by DLW in this work will expand the toolkit of methods for patterning LEDs and lasers of colloidal QWs, which is currently a very rapidly progressing direction of research.

In our experiments, we studied the laser structuring of both spin-coated (SC) and oriented self-assembled (SA) films of CdSe/CdZnS nanoplatelets, of which individual quantum structure and film structure are schematically shown in Fig. 1(a). All details on the synthesis protocols and film deposition processes are given in the supplementary material.

The SC method is more versatile and makes it possible also to obtain thick films. The simplicity, speed, and ease of thickness control render this method as one of the most commonly used coating techniques for creating thin films from a vast range of materials. For further investigation by the SC method, a sample with the film of average thickness of 110 nm on a glass substrate was created and hereinafter is called as “SC.”

The SA method, on the other hand, makes it possible to create the films monolayer by monolayer with high precision of film thickness with much lower roughness. This feature makes this method attractive for the purpose of increasing the luminescence characteristics and outcoupling efficiency for lowering the lasing thresholds.

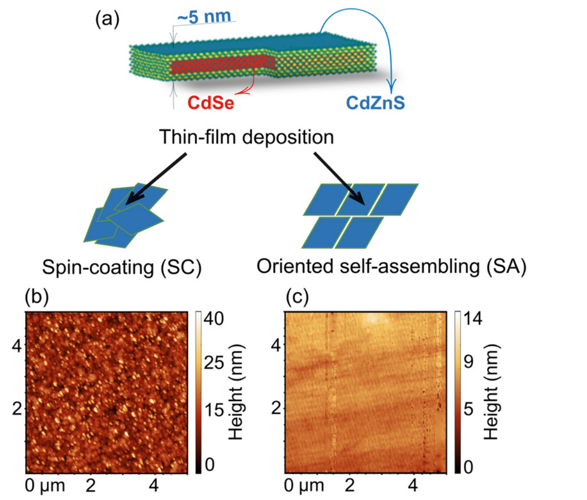


FIG. 1. (a) Schematic illustration of a colloidal CdSe/CdZnS nanoplatelet and its SC and SA film deposition methods. (b) AFM image of SC film and (c) AFM image of SA film.

Here, we use a SA method specifically developed to orient the NPLs in face-down configuration.[17] Although the SA method is also scalable, in principle, the one we employ here is specific to the NPLs used and has its peculiarities. As each new layer is added, the irregularities and discontinuities in the underlying layers are accumulated and contribute to the final inhomogeneity. This fact makes the SA method significantly more time-consuming compared to the SC method. A sample consisting of nine monolayers of CdSe/CdZnS NPLs with an average film thickness of 50 nm on a glass substrate, hereinafter referred to as “SA,” was created using this method. A significant decrease in the roughness amplitude from 5 nm for the SC to 1 nm for the SA film was confirmed by atomic-force microscopy (AFM) imaging [Figs. 1(b) and 1(c)]. Morphological characterization of the surface was performed on an AFM setup Aist-NT “SMART” with golden silicone probes “NSG01” (TipsNano).

Structures of different dimensions on such films can be created by DLW,[18] which is a fast and high-throughput surface modification method. Femtosecond laser radiation causes various ultrafast phenomena on a surface of such obtained film: melting, shock-wave generation, ablation, cooling, resolidification, and redeposition, allowing one to create a plethora of nano- and micro-structures.[19] Schematic illustration of our experiment on DLW surface nanostructuring is shown in the inset of Fig. 2(a). The creation of 1D gratings was performed on a Pharos Light Conversion setup with a pulse energy of up to 10 $\mu$J, with a duration of 200 fs. The laser wavelength for the modification was 1030 nm and the sample displacement rate was 50 $\mu$m/s. The Mitutoyo objective 100× with NA 0.7 was used for focusing laser beam onto a spot with the radius $R_{1/e} \approx 618$ nm.

The values of damage thresholds for different films [Fig. 2(b)] were estimated by applying different number of laser pulses per single spot of the film and sweeping their fluence in a broad range. The threshold fluence for a particular regime was determined when the optical power absorbed within the laser focal spot of 1 $\mu$m in diameter created a modification line that was clearly observable by an optical microscope with a 100× objective.

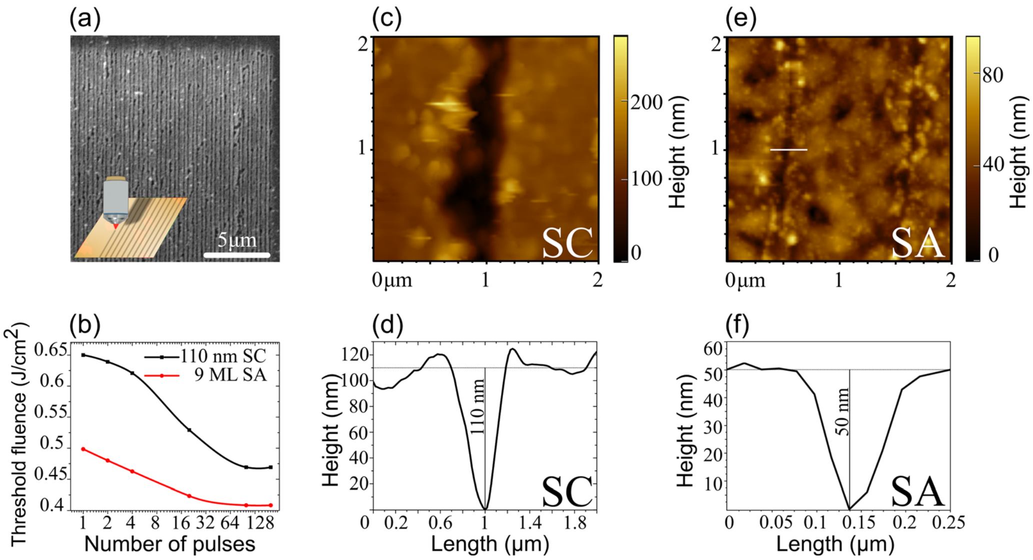


**FIG. 2.** (a) SEM image of a nanostructure with a period of 400 nm on the SC NPL film. Inset: schematic illustration of the DLW method applied for thin-film nanostructuring. (b) Measured observable damage thresholds for SC 110-nm NPL film and SA 50-nm NPL film. AFM images and 1D averaged profiles of the lines created on two samples: the SC film by 20 focused laser pulses with a fluence of 529 mJ/cm$^2$ (c) and (d) and the SA film by 200 focused laser pulses with a fluence of 408 mJ/cm$^2$ (e) and (f).

Analysis of the position and shape of the curves (see Fig. S1 in the supplementary material) allows us to estimate the characteristics of heat dissipation during the ablation depending on the method of film deposition. When the number of laser pulses per unit surface is increased, this threshold expectedly decreases. The observable damage threshold saturation for large number of pulses is consistent with the previous reports on thin films made of other materials.[20,21] Using the obtained information on the observable damage thresholds, we chose the optimal modification regime for each type of film (see Fig. S2 in the supplementary material). The AFM studies confirmed the full-depth modification of the film above the damage threshold [Figs. 2(c)–2(f)].

In order to design a periodic nanostructure for our NPL films, we used numerical modeling with Fourier modal method.[22] In the simulation, we optimized the parameters of the 1D grating (period and fill factor) to match the spectral position of the optical modes with the emission band of the NPL film. It is worth noting that the spectral position of the emission peak for the SC and SA samples was slightly different (670 vs 635 nm). The observed red-shift of the emission peak for the SC sample is caused by a different size fraction of NPLs in the solution used for the preparation of this film. Furthermore, the larger thickness of SC sample leads to stronger photon recycling effect,[23] which also contributes to the spectral shift of the peak, compared to the SA sample. In our simulations, we used the refractive index of the NPLs film extracted from ellipsometry measurements (see Table S1 in the supplementary material). The refractive index of the glass substrate was set to 1.5. The simulations revealed that high-Q optical modes are excited near the emission band of both 110 nm thick SC film and 50 nm thick SA film for the grating periods within the range of 400–450 nm. For these periods, the structure exhibits two counter-propagating Bloch modes that are crossed at wavenumber $k_x = 0$ (i.e., at Γ-point). For the fill factor feasible for our DLW process, there is no splitting of these modes at Γ-point. With further optimization of the groove width, the same design may possibly enable the splitting of the modes into symmetric and antisymmetric branches[24] and excitation of bound-states-in-the-continuum that can be utilized for low-threshold lasing. The reflection spectra of nanostructures with periods of 400, 435, and 450 nm were calculated on NPL films with thicknesses of 110 and 50 nm (Fig. 3).

To confirm the presence of the optical modes and PL enhancement properties, angle-resolved PL measurements in the back focal plane (BFP) were performed. For this purpose, the nanostructures with periods of 400, 435, and 450 nm were created on both types of samples. Low-noise liquid-nitrogen-cooled imaging CCD camera (Princeton Instruments SP2500+PyLoN) coupled with a slit spectrometer allowed us to make angle-resolved PL measurements in a back-focal-plane. The sample was excited by 200-fs laser pulses at a wavelength of 405 nm from a femtosecond laser system (Pharos) with a collinear optical parametric amplifier (Orpheus-HP). The laser beam was focused in the back focal plane of the objective to achieve the homogeneous exposition.

In all panels of Fig. 3, reflection spectra are mapped as a function of the normalized in-plane wavenumber $k_x/k_0$. Changing the period of the nanostructure affects the position of the modes—when the period increases from 400 to 450 nm, the red-shift is observed in both SA and SC samples. When the modes spectrally overlap with the photoluminescence band, a noticeable enhancement is observed due to the presumably higher Purcell factor for the emitted light coupled to the optical modes.[25] The PL enhancement at the mode resonance in Γ-point was up to 3 and 1.8 times for SA and SC films, respectively (see Fig. S3 in the supplementary material). This difference in the enhancement factors is likely caused by higher quality for the SA film, thinner modification lines, and lower scattering losses for the excited modes. Also, the enhanced emission directed at the angles close to the

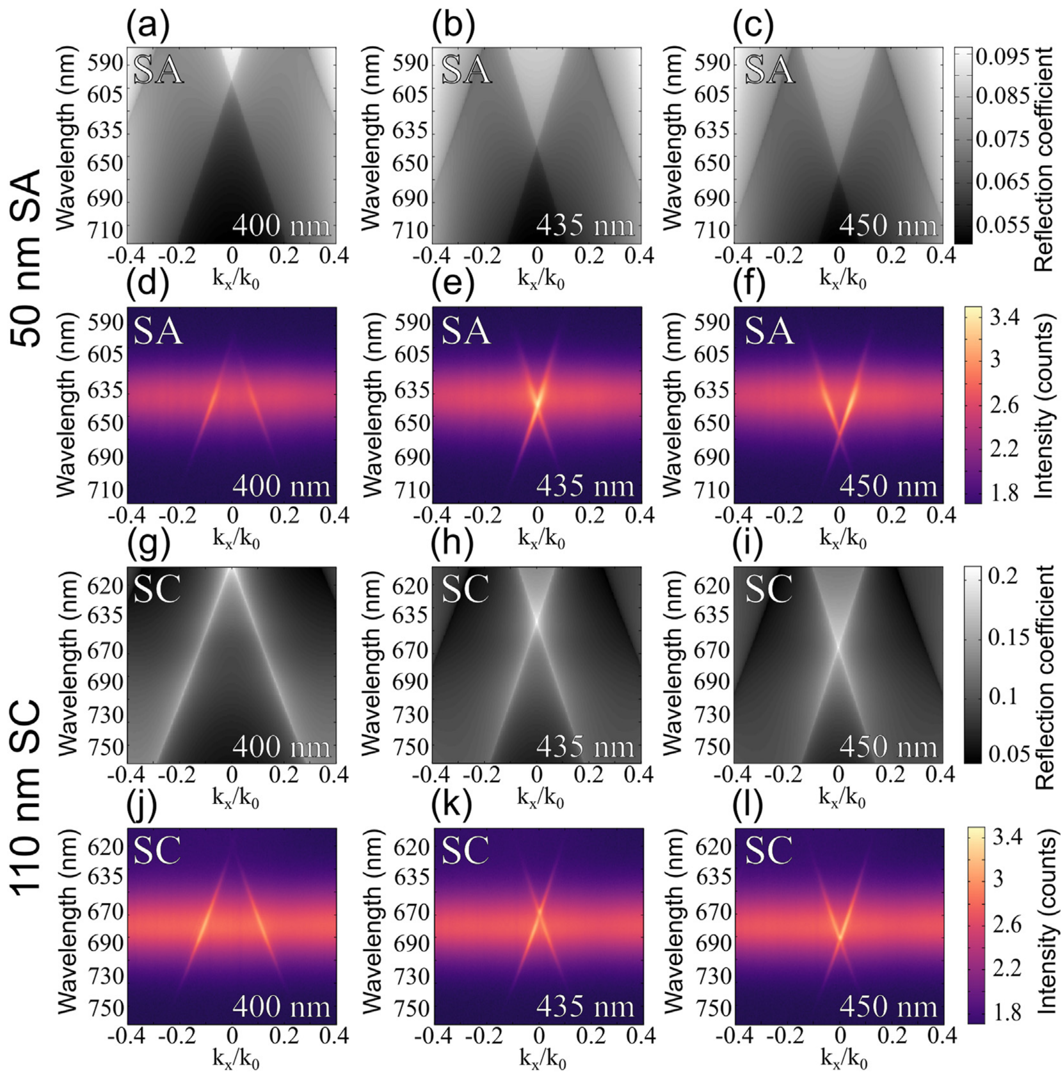


**FIG. 3.** Angle-resolved BFP imaging simulated and measured showing resonant modes for comparison between the simulation and experiment results on a nanostructured NPL film with periods of 400 nm (first line), 435 nm (second line), and 450 nm (third line): (a)–(f) the SA samples and (g)–(l) the SC samples.

Γ-point might be useful for the directional outcoupling of the LEDs based on such NPL films.

To summarize, we have shown a simple yet versatile method for direct femtosecond laser nanostructuring of the light-emitting films deposited from colloidal solution CdSe/CdZnS core/shell NPLs. The method is useful for creating structures on large area and allows for the modification of the entire thickness of the film. The observation of significant optical enhancement from the structured surface confirms the fact that the ligands between each NPL suppress the propagation of heat during laser surface modification protecting the remained nanocrystals against the harmful overheating and allow the creation of high-quality structures. The approach developed in this work will be useful for the creation of efficient light-emitting devices with directional emission outcoupling as well as for advanced designs of distributed feedback lasers including those based on bound states in the continuum with lower thresholds.

See the supplementary material for materials, synthesis of NPLs, film deposition processes, morphological and optical properties of NPLs film, and created resonant structures.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

## Author Contributions

**Ruslan Azizov:** Formal analysis (lead); Investigation (equal); Visualization (lead); Writing – original draft (lead). **Ivan S. Sinev:** Conceptualization (equal); Investigation (equal); Writing – review & editing (equal). **Furkan Isik:** Investigation (supporting). **Farzan Shabani:** Investigation (supporting). **Anatoly P. Pushkarev:** Investigation (supporting). **Iklim Yurdakul:** Investigation (supporting). **Savas Delikanli:** Investigation (supporting). **Hilmi Volkan Demir:** Conceptualization (equal); Supervision (equal); Writing – review & editing (equal). **Sergey Makarov:** Conceptualization (equal); Supervision (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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