

Two- and one-dimensional light propagations and gain in layer-by-layer-deposited colloidal nanocrystal waveguides

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Optical waveguides containing high percentages of colloidal nanocrystals have been fabricated by layer-by-layer deposition on planar and patterned glass substrates. The two- and one-dimensional waveguidings in these structures are demonstrated by propagation loss experiments. The experimental results obtained for various film thicknesses and widths of the waveguide stripes together with simulations of the light propagation indicate that the losses are dominated by surface roughness. The variable stripe length method is used to determine the optical gain of 230 cm^{-1} from the amplified spontaneous emission. This high value makes the authors' waveguide structures very promising for applications in amplifiers and lasers with reduced threshold powers. © 2006 American Institute of Physics. [DOI: 10.1063/1.2354433]

Wet-chemical methods enable the synthesis of nearly monodisperse colloidal semiconductor nanocrystals (NCs) with dimensions in the strong quantum confinement regime,¹ giving widely size tunable room temperature luminescence² with quantum efficiencies close to unity.³ Their solubility in various solvents allows their incorporation in different matrices.⁴ These favorable characteristics provide a flexible platform for the development of integrated photonic devices based on NCs, including optical amplifiers and lasers operating at room temperature. The main difficulty in achieving NC-based lasing is the very efficient nonradiative Auger recombination,⁵ so that laser operation is achieved so far only with pulsed excitation.⁶ Strategies to improve the laser performance are (a) to increase the NC concentration in the active layer,⁷ (b) the use of high-finesse optical feedback structures,⁶ and (c) the optimization of the optical waveguides. While the properties of optical waveguides containing Si nanocrystals fabricated by implantation have been studied in detail,⁸ for waveguides containing colloidal NCs only the principal operation has been demonstrated.⁹ Therefore, here we present a systematic investigation of two-dimensional (2D) and one-dimensional (1D) waveguides (WGs), optically activated by strongly luminescent colloidal CdTe NCs synthesized according to Ref. 10. To obtain structures with smooth surfaces and high NC volume fractions the layer-by-layer deposition technique¹¹ is applied. The waveguides exhibit propagation loss coefficients less than 1 cm^{-1} , depending on the thickness of the WGs. The losses are only weakly dependent on the width of the 1D WGs and are determined by the surface roughness. The amplified spontaneous emission, excited by femtosecond pulses, evidences a high optical gain of 230 cm^{-1} , showing that our WGs are highly suitable as active components in NC-based lasers and amplifiers.

The NC WGs are fabricated by controlled deposition of CdTe NC/polymer films onto glass substrates by the layer-by-layer assembly method.¹¹ This simple technique makes use of the alternating adsorption of (sub)monolayers of oppositely charged molecules or nanoparticles. In particular, we use positively charged poly(diallyldimethylammonium chloride) (PDDA) molecules in combination with negatively surface-charged CdTe NCs, each provided in aqueous solutions with appropriately adjusted *pH* values. The total film thickness is controlled by the number of PDDA/CdTe NC bilayers and by the deposition time for each monolayer. For a film with 40 bilayers we obtain a typical thickness of 170 nm. Since the effective thickness of a PDDA molecule (approximately 1 nm) is several times smaller than that of the used CdTe NCs with a diameter of 3.2 nm,¹² we obtain exceptionally high NC concentrations close to 60% in volume as determined from the optical density of the films. By the use of PDDA with high molecular weight ($M_r = 500\,000$) very smooth and shiny film surfaces are obtained with a roughness in the order of 4 nm, as demonstrated in Fig. 1(a) by the atomic force microscope (AFM) line profiles of a CdTe/PDDA film with 40 bilayers. For the 1D WGs, the NC/polymer bilayer films are deposited on substrates, patterned with grooves with widths of 5, 10, 20, and 40 μm and a length of 2 cm. The 450 nm deep grooves are wet chemically etched by making use of a 30 nm thick Cr layer as etch mask. The waveguiding properties of the NC/polymer films are studied by propagation loss measurements using the NC luminescence. An Ar-ion laser operating at 514 nm is used to excite the NCs from a direction perpendicular to the sample surface, while the photoluminescence (PL) emitted in lateral direction is collected from the sample edge by a microscope objective. For detection, a Si-diode array is used in combination with a 1/8 m spectrograph. The PL spectra are recorded as a function of the distance *z*, measured between the excitation spot and the edge of the sample [see inset in Fig. 1(c)].

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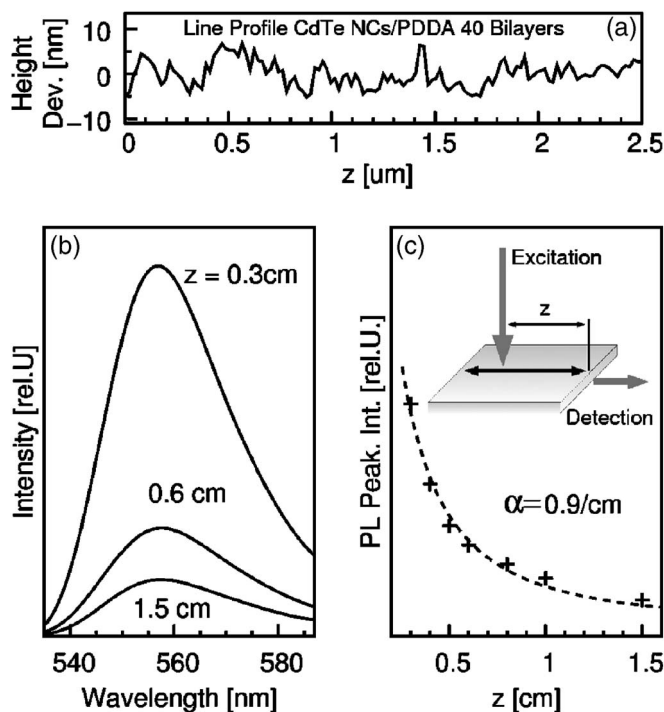


FIG. 1. (a) Line profile of a 40 bilayer thick layer-by-layer assembled CdTe NC/PDDA film determined by atomic force microscopy. (b) PL spectra and (c) PL peak intensities of the two-dimensional nanocrystal waveguides collected in lateral direction for various propagation distances (see inset).

In aqueous solution, the used CdTe NCs exhibit a single PL peak with a full width at half maximum (FWHM) of 36 nm. The PL peak is Stokes shifted in respect to the first excitonic absorption peak by 30 nm. This large Stokes shift is essential for the propagation of the NC PL in the WGs, which is only possible within the transparent energy region of the NCs. As shown in Fig. 1(b), for the 2D WGs the PL spectra collected in lateral direction exhibit a strongly asymmetric shape and a FWHM of 28 nm, which is reduced with respect to that observed for the solution. The reason for these facts is the efficient PL reabsorption at the high energy tail of the PL spectrum. For the lower energy part of the PL spectrum, propagation of the PL emission is observed over relatively long distances. Figure 1(c) shows the PL spectra for various distances z between excitation point and sample edge, revealing that increasing z results in a decrease of the PL intensity, regardless of the emission wavelength. Therefore, it is sufficient to examine the dependence of the peak intensity, as is given in Fig. 1(c). There, the experimental data are fitted by a function which is proportional to $1/z e^{-\alpha z}$ (dashed line). Here the factor $1/z$ accounts for the intensity drop of a radial wave within a 2D slab. The exponentially decaying part is ascribed to the losses in the WG. Here the loss coefficient α takes into account absorption within the slab as well as scattering at the surfaces. The scattering losses are determined by the surface roughness of the film. For the film consisting of 40 NC/PDDA bilayers we find an α of 0.9 cm^{-1} so that these films are an appropriate material for waveguiding devices with dimensions up to several centimeters.

For most of such devices, waveguiding in one direction is required. Since structuring of NC/PDDA films is not well developed, we investigate the possibility to obtain 1D waveguiding in NC/PDDA films deposited on patterned glass

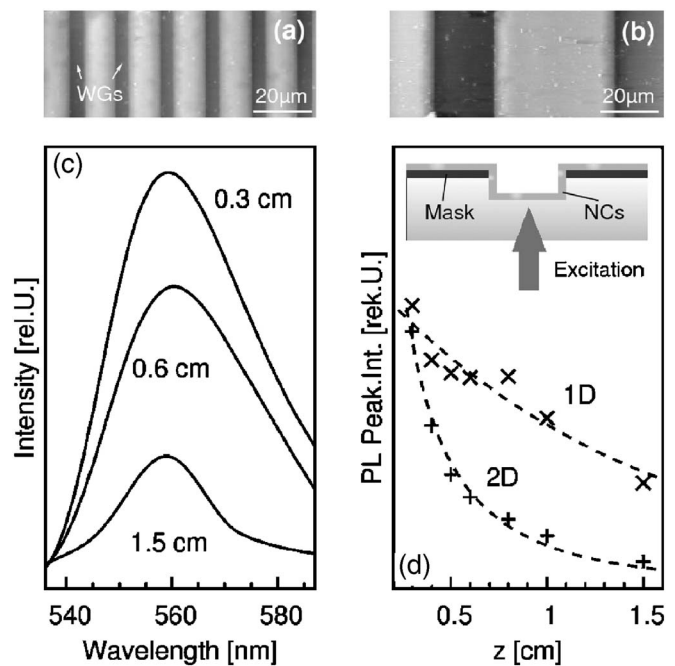


FIG. 2. Atomic force micrograph of nanocrystal waveguides prepared on patterned substrates with groove widths of (a) 5 and (b) 20 μm . (c) PL spectra observed at various propagation distances for the waveguides shown in (b). (d) Comparison of peak PL decay between the 1D and 2D waveguides. Inset: Sketch of the sample structure.

substrates. As shown by the AFM images in Figs. 2(a) and 2(b), this results in WG stripes with rather smooth edges. The laser excitation in this case is performed through the substrate to excite the NCs only in the grooves. As sketched in the inset of Fig. 2(d), the NCs on the ridges are masked by the Cr layer which is used also as etch mask. The luminescence spectra observed for the NCs in the grooves [Fig. 2(c)] exhibit a very similar shape than those for the planar films. The decay of the PL intensity with increasing z , however, is by far smaller as in the 2D case. This is shown in Fig. 2(d), where the dependence of the peak PL intensities on z is compared for the 1D and the 2D case. For the 1D, the decay can be fitted by a single exponential, without the $1/z$ prefactor, which we quote as an indication for a truly 1D waveguiding. This conclusion is confirmed by the microscope image of the sample edge shown as inset in Fig. 3(a). There, the row of bright spots represents the well separated emission from the end faces of more than ten individual WGs.

To clarify the origin of the WG losses, we investigate 1D WGs with various layer thicknesses and widths. Reducing the thickness from 40 to 10 NC/PDDA bilayers results in an increase of the loss coefficient by a factor of 2 [see Figs. 3(a) and 3(b)]. This is almost independent of the groove width, varied between 5 and 40 μm . Remarkably, for the 1D WGs, the same loss coefficient is obtained as for the planar films. Thus, the roughness of the grooves is negligible in comparison with that of the NC/PDDA surfaces. To support our conclusions we have calculated the distribution of the electromagnetic fields in our WGs, modeled as stripes with effective refractive indices as determined from spectroscopic ellipsometry. As shown in Fig. 3(c), in such WGs with thicknesses below 200 nm, a single optical mode is observed. With reducing film thickness, the mode spreads more and more out of the active layer, so that the contribution of the surface roughness becomes increasingly dominant, which is

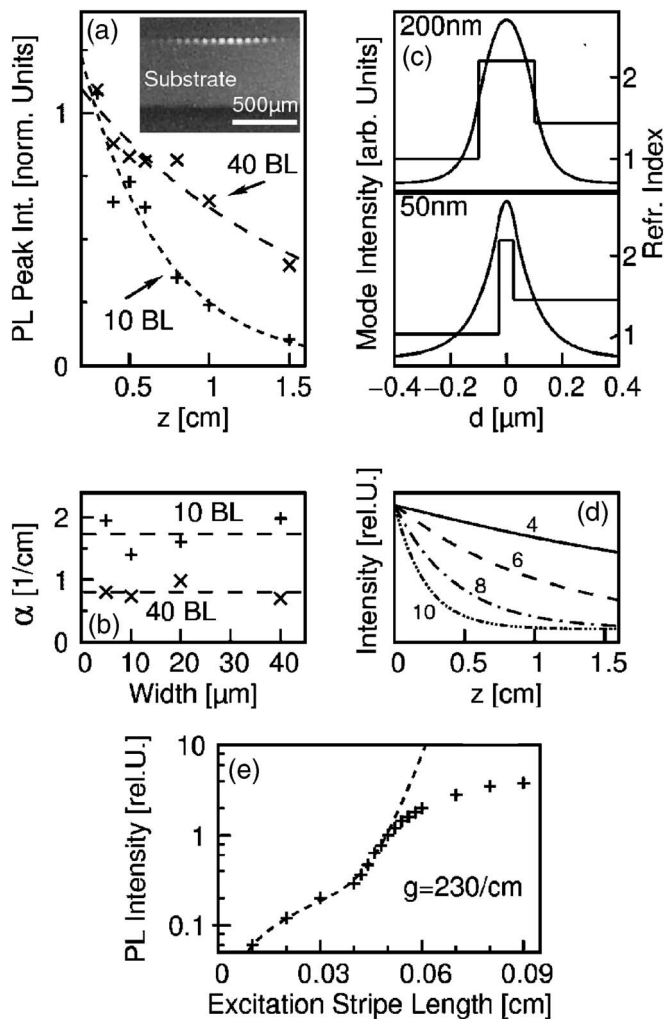


FIG. 3. (a) PL decay for two nanocrystal film thicknesses. The inset shows a micrograph from the sample edge whereby the bright spots are the guided PL emission. (b) Waveguide loss coefficients as a function of the waveguide width. (c) The effective refractive index profiles of the waveguides together with the calculated mode-field distributions for 50 and 200 nm thick NC/PDDA films. (d) Simulated light propagation for surface roughnesses varying between 4 and 10 nm. (e) Emission intensity observed under pulsed excitation for various excitation stripe lengths.

in agreement with our experimental findings. To quantify the losses due to surface roughness we have performed finite difference time domain simulations, assuming no absorption in the NC/PDDA layer. The results of these simulations, shown in Fig. 3(d), predict a cubic increase of α with increasing surface roughness. For the surface roughness as determined by the AFM line profile in Fig. 1(a), the simulation gives a value for α which is about half of the experimental one. This small discrepancy indicates finite but small absorbance of the guided light by the NCs and might also account for thickness variations of the films, taking place on size scales larger than those typically probed by the AFM.

Our WGs provide a high optical gain under intense excitation, achieved by a frequency-doubled regenerative amplified Ti:sapphire laser, giving 120 fs pulses at a wavelength of 390 nm. The pump pulses are focused onto the NC WGs with a cylindrical lens to a narrow stripe and the emission

from the sample edge is detected. The PL intensity is plotted in Fig. 3(e) as function of the excitation stripe length (l). It shows a linear increase up to 0.04 cm, abruptly followed by an exponential increase up to 0.05 cm. This typical behavior for amplified spontaneous emission can be well fitted by the expression $I=Al+B(e^{gl}-1)/g$,⁶ where A and B are fitting constants and g is the biexciton modal gain. Above a stripe length of 0.05 cm the curve levels off due to saturation effects.⁶ The fit results in a modal gain of the WG mode of $g=230\text{ cm}^{-1}$. This value is indeed somewhat higher than obtained so far for films containing CdSe NCs,⁶ confirming that the high NC content in our structures is suitable for the development of NC-based laser structures with improved threshold powers.

In summary the high potential of layer-by-layer deposited NC/PDDA films for applications in optical devices is demonstrated. In these films, deposited on planar as well as on patterned glass substrates, two- and one-dimensional waveguidings are observed with penetration length of several centimeters. Under pulsed excitation a high optical gain is obtained as a result of the high NC concentration in the films, which is of special benefit for optical amplifiers and lasers.

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