

Lateral Patterning of Luminescent CdSe Nanocrystals by Selective Dewetting from Self-Assembled Organic Templates

Nan Lu,^{†,||} Xiaodong Chen,[†] Daniel Molenda,[†] Andreas Naber,[†] Harald Fuchs,[†] Dmitri V. Talapin,[‡] Horst Weller,[‡] Josef Müller,[§] John M. Lupton,[§] Jochen Feldmann,[§] Andrey L. Rogach,^{*,§} and Lifeng Chi^{*,†,||}

Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, Center for Nanotechnology (CenTech), Gievenbeckweg 11, 48149 Münster, Germany, Institut für Physikalische Chemie, Universität Hamburg, Bundesstr. 45, 20146 Hamburg, Germany, Sektion Physik und CeNS, Ludwig-Maximilians-Universität München, Amalienstr. 54, 80799 München, Germany, and Key Lab of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 130023 Changchun, P.R. China

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ABSTRACT

We present a simple nonlithographic approach to arrange luminescent CdSe and core/shell CdSe/ZnS nanocrystals into large area periodic lateral patterns. Selective deposition onto organic channel-like templates fabricated by the Langmuir–Blodgett technique is achieved by anisotropic dewetting of the nanocrystal carrier solvent. Lateral patterning over large areas of several square centimeters is demonstrated on a time scale of a few minutes. The filling fraction of nanocrystals within the deposited channels is controlled by their concentration in solution as well as the deposition time. Prolonged growth leads to the formation of island-like aggregates or almost continuous lines. Nanocrystals preserve their strong luminescence when deposited into channels, which makes the fabricated periodic structures promising for optoelectronic applications.

Semiconductor and metal nanocrystals (NCs) are attractive building blocks for fabricating so-called artificial solids,^{1,2} which may provide a basis for novel photonic, electronic and magnetic devices.^{3–8} For a variety of applications, the ability to arrange NCs into ordered structures on solid substrates is of a great importance. Various approaches have been proposed to provide the lateral patterning, including e-beam or ion-beam lithography^{9,10} and microcontact printing techniques.¹¹ The most important requirement for industrial applicability and scalability is, however, that the technique employed be both simple and reliable and suited to large area processing, allowing the formation of large scale periodic patterns of NCs in a short time. One of the attractive solutions relies on the interplay of hydrophobic and hydrophilic interactions between the NCs and the substrate and utilizes organic templates, which are pre-patterned lithographically,¹² by using self-assembled monolayers¹³ or by applying Langmuir–Blodgett (LB) techniques.^{14–16}

In this letter we present a patterning technique that allows the alignment of luminescent CdSe and core/shell CdSe/ZnS NCs into large area periodic lateral structures. Selective deposition of NCs onto organic channel-like templates fabricated by the LB technique is achieved by anisotropic dewetting of the NC carrier solvent (1-phenyloctane). The filling fraction of NCs within the channels is controlled by their concentration in solution and the deposition time.

CdSe and CdSe/ZnS NCs used in this work were synthesized according to the previously published procedure¹⁷ in a three-component coordinating solvent mixture of hexadecylamine, trioctylphosphine, and trioctylphosphine oxide. Figure 1 shows absorption and photoluminescence spectra (black lines) of CdSe core particles (5.5 nm diameter) and CdSe/ZnS core/shell particles (5 nm diameter), which emit around 630 and 525 nm, respectively. The NCs are precipitated from the crude solutions by methanol and redissolved in 1-phenyloctane to yield solutions with concentrations ranging from 0.1 mg/mL to 5 mg/mL. We have previously reported a technique of generating submicrometer periodic patterns without involving any lithographic steps by exploiting wetting instabilities, which occur when monomolecular layers are transferred onto a solid substrate.¹⁴ Lateral periodic patterns consisting of stripes composed of L- α -dipalmitoyl-phosphati-

* Corresponding authors. E-mail: andrey.rogach@physik.uni-muenchen.de (ALR); chi@uni-muenster.de (LFC).

[†] Westfälische Wilhelms-Universität Münster and Center for Nanotechnology (CenTech).

[‡] Universität Hamburg.

[§] Ludwig-Maximilians-Universität München.

^{||} Jilin University.

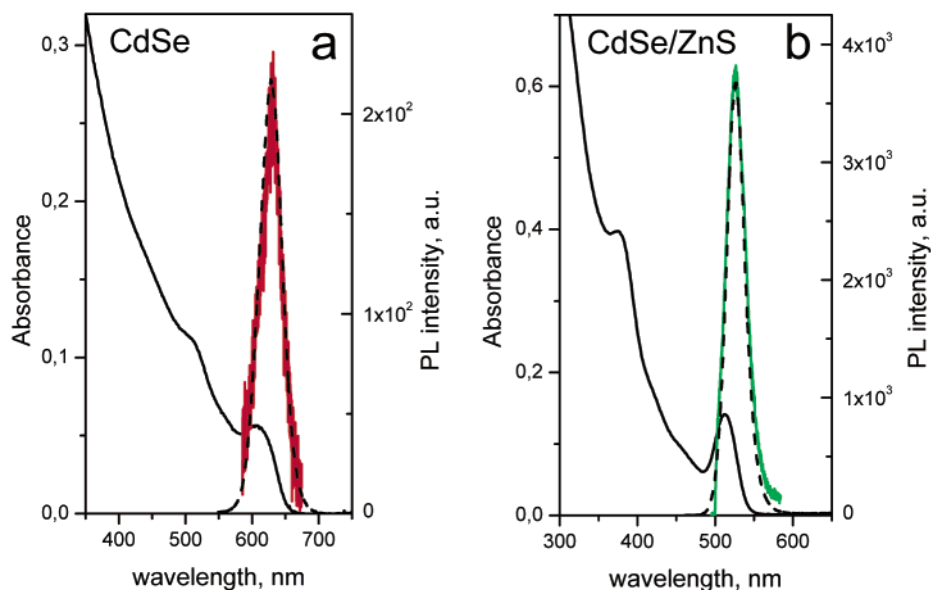


Figure 1. Absorption (black solid lines) and emission (black dashed lines) spectra of (a) 5.5 nm CdSe NCs and (b) 5 nm CdSe/ZnS NCs dissolved in 1-phenyloctane, which were used for the fabrication of lateral patterns. The emission spectra measured on approximately 10 channels of the same CdSe (red solid line) and CdSe/ZnS (green solid line) NCs patterned on the DPPC template are also shown.

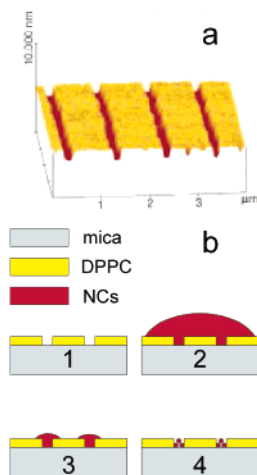


Figure 2. (a) Topographic SFM image of self-assembled channels between DPPC stripes on a mica surface. (b) Schematic outline of the four steps used to pattern luminescent NCs into the channels. Covering the patterned mica substrate with NC solution leads to selective dewetting from the DPPC layer and preferred crystal assembly between the DPPC stripes.

dicholine (DPPC) of 700–900 nm (depending on preparation conditions) width and 2 nm (i.e., monomolecular) height separated by 150–200 nm wide channels of bare mica surface are fabricated by the LB technique on mica substrates as previously reported,¹⁴ and serve as templates for selective deposition of NCs. The length of the stripes is limited only by the substrate size and is 2 cm in our experiments. Figure 2a shows a scanning force microscope (SFM) image¹⁸ of a small region of a typical patterned substrate. NCs are deposited by dropping the solutions of NCs in 1-phenyloctane on the DPPC-structured mica substrates, which provides a contact angle of ca. 40°. The NCs accumulate in the bare mica channels due to selective dewetting from the DPPC strips, which is followed by removal of the solution from the sample surface with filter paper after 5–15 min and

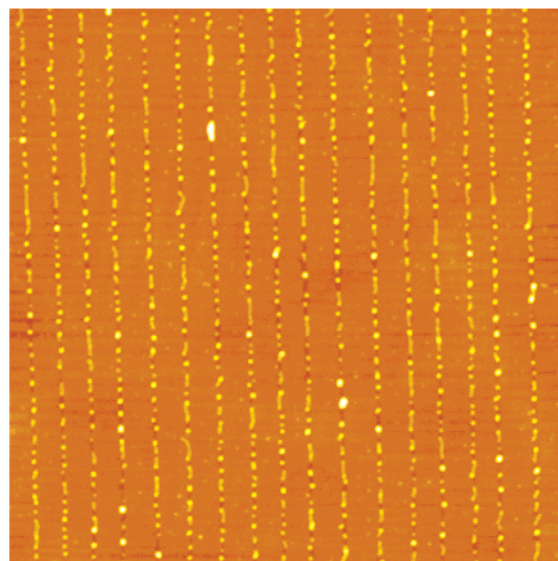


Figure 3. Typical topographic SFM image of CdSe NCs deposited on a DPPC template (0.5 mg/mL solution, 5 min deposition time). X, Y: 20 μ m.

subsequent drying of the samples in air or under nitrogen flow. This selective dewetting of the NC solution can be understood by considering the difference in wettability owing to different surface energies for the carrier solvent between mica channels and DPPC stripes.^{14,16} The process steps are summarized schematically in Figure 2b. We note that the DPPC stripes exposed to 1-phenyloctane remain stable and do not change their morphology over prolonged periods of time.¹⁴

Figure 3 shows an SFM image of a typical sample, which demonstrates that most of the NCs are deposited uniformly into the channels, with only a few aggregates of NCs visible as bright spots on top of the organic layer regions which form broad stripes. The DPPC stripes remain virtually unwetted by 1-phenyloctane, which drives the NC solution

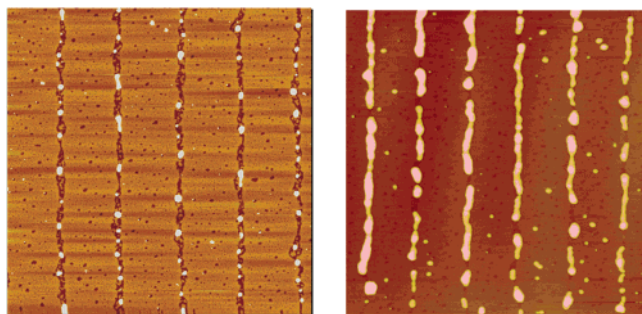


Figure 4. Topographic SFM images of patterned CdSe NCs at high magnification, demonstrating different types of arrangement of NCs within the channels depending on the solution concentration. Left panel: low concentration (0.1 mg/mL, 5 min deposition time); right panel: high concentration (5 mg/mL, 5 min deposition time). X, Y: 5 μ m.

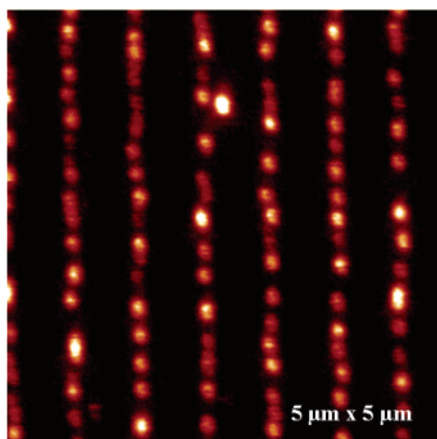


Figure 5. SNOM image of a luminescent pattern of CdSe NCs (0.5 mg/mL, 5 min deposition time).

to fill the channels between the organic stripes. The filling fraction of NCs within the channels is determined by their concentration in solution and the duration of contact between the solution and the substrate. At a low concentration of NCs in solution (0.1 mg/mL) and a deposition time of 5 min, the NCs tend to assemble into spots, as shown in the SFM image in Figure 4a. The height of these spots is measured to be ~ 5 nm, which corresponds to the diameter of a single NC. Increasing the concentration of the NC solution to 5 mg/mL leads to an increased density of the deposited NCs, most of which assemble into almost continuous lines (Figure 4c). The height of the lines was measured to be 14 nm, indicating that at this stage the NCs are deposited on top of each other, forming films approximately three monolayers in thickness.

To demonstrate that the NCs retain their favorable luminescence properties after patterning, scanning near-field optical microscopy (SNOM) measurements were carried out.¹⁹ Figure 5 shows a SNOM image measured on a sample assembled in a deposition time of 5 min from a 0.5 mg/mL solution. Strongly luminescent spots are clearly identified within the channels, which coincide with the topographic images obtained with the SFM (Figure 3). To confirm that the luminescent spots indeed correspond to assemblies of NCs we measured the PL spectra using a micro-PL setup.²⁰ In this case the spatial resolution was limited to roughly 1 μ m, so

that individual lines could not be resolved. Emission spectra measured for approximately 10 channels in parallel are shown in Figure 1 for both bare CdSe cores and CdSe/ZnS core/shell particles and unambiguously demonstrate that the luminescence of the nanostructured surface originates from the NCs deposited. The emission intensity of the core/shell CdSe/ZnS NCs in the mica channels is more than an order of magnitude larger than that of the CdSe NCs, which is in a good agreement with the relative quantum yields determined in solution measurements. It is important to note that the NCs keep their luminescence even though they form aggregates in channels. The selective deposition technique introduced here therefore provides a possibility of fabricating light-emitting periodic patterns on a large scale. In this context it is important to note that the lattice period of the DPPC stripes can be adjusted freely (by, for example, varying the temperature¹⁴) and may therefore be matched to the emission wavelength of the NCs.

In summary, we have presented a simple nonlithographic method for patterning luminescent semiconductor NCs into periodic lateral structures over large areas (several cm²) within a few minutes. The driving force for selective deposition of NCs is an anisotropic dewetting of the organic templates by the NC carrier solvent. SNOM and micro-PL measurements demonstrate that the deposited NCs retain their luminescence properties, which has important application potential. Nanostructure fluorescent templates are useful in biological assays, but could also form the basis for novel distributed feedback lasing structures.²¹ In particular, we note that wavelength scale patterning of the emissive layer drastically enhances the light out-coupling efficiency,²² which is of importance to a range of optoelectronic devices such as light-emitting diodes.

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- (18) SFM images were obtained with a commercial instrument (Digital Instruments, Nanoscope IIIa, Dimension 3000, Santa Barbara, CA) running in tapping mode. Si cantilevers (Nanosensors) of spring constants 250–350 kHz were used.
- (19) SNOM measurements have been done with a home-designed instrument [see ref 23]. The SNOM probe was prepared according to ref 24. A 488 nm laser was used as excitation source. For fluorescence imaging, two edge filters (Nikon, 515IF), and a color glass BG39 (Schott) were used to suppress the excitation wavelength and allow the light beyond 525 nm going through.
- (20) Samples were mounted in a vacuum chamber (cryostat) and evacuated down to 10^{-5} mbar. For excitation, the 457.9 nm line of a cw argon ion laser was used. The excitation density on the sample was approximately 25 W/cm². Luminescence from an area of approximately $5\ \mu\text{m} \times 5\ \mu\text{m}$ containing roughly 10 channels was recorded using an epifluorescence microscope with a long distance objective lens (NA: 0.55). The light was spectrally resolved with a monochromator and directed to a cooled CCD. The integration time for all spectra was 10 s.
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