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Hierarchical Luminescence Patterning Based on Multiscaled Self-Assembly

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Hierarchical organization is the most conspicuous property of cells and organisms, and also the most elusive.¹ Similarly, in nanotechnology, the hierarchical organization of nanostructures across extended lengthscales is a key challenge in the design of integrated functional materials,² e.g., electronic nanodevices.^{3,4} A promising strategy to organization of the nanostructures is based on surface patterning, which could be realized by top-down and bottom-up techniques.⁵

The surface patterning with luminescent micro- and nanoscopic features is of great interest for applications in photonics,^{6,7} optoelectronics,^{8,9} biochip detection,¹⁰ and biosensor arrays.¹¹ The fabrication of hierarchical luminescence patterns is a fundamental step for the integration and registration of photonic nanodevices. The current methods for fabrication of nanoscale hierarchical patterns, such as e-beam lithography and deep-UV photolithography, are very costly and energy consuming. This inspires the search for bottom-up techniques based on self-assembly phenomena because of their simplicity and compatibility with heterogeneous integration processes.¹²

Herein, we describe a procedure for fabricating a hierarchical luminescence pattern based on multiscaled self-assembly.¹³ First, we generate two levels of hierarchical luminescence patterning using self-assembly. The third-level pattern has been obtained by exposing samples to light through a shadow mask. For this step, we make use of the photoinduced enhancement of fluorescence of CdSe nanocrystals (NCs)^{14–16} and photobleaching of dyes. The entire process is inexpensive and high-throughput and can be applied to different combinations of materials and shadow masks.

Our approach combines molecular self-assembly with a template-assisted self-assembly, as schematically shown in Figure 1. The first-level pattern of green-emitting stripes with submicrometer lateral dimensions was obtained by transferring mixed monolayers of 1- α -dipalmitoyl-phosphatidylcholine (DPPC) and 2-(4,4-difluoro-5-methyl-4-bora-3a,4a-diaza-*s*-indacene-3-dodecanoyl)-1-hexadecanoyl-*sn*-glycero-3-phosphocholine (BODIPY) (0.5 mol %) onto a mica surface by means of a Langmuir–Blodgett (LB) technique due to a substrate-mediated microphase separation and a periodic oscillation of the meniscus at the three-phase contact line.¹⁷ A droplet of red-emitting CdSe NCs in 1-phenyloctane solution was dripped onto a self-assembled first-level pattern (Figure 1a). Red-emitting CdSe NCs (5.5 nm diameter, emission peak at ~ 640 nm) were synthesized according to the previously published procedure.¹⁸ The CdSe NCs were precipitated from the crude solutions by methanol and redissolved in 1-phenyloctane to yield ~ 0.1 mg/mL solutions.

After keeping the droplet of CdSe NCs on the self-assembled patterns for 5 min (Figure 1b), the droplet was removed by a pipet

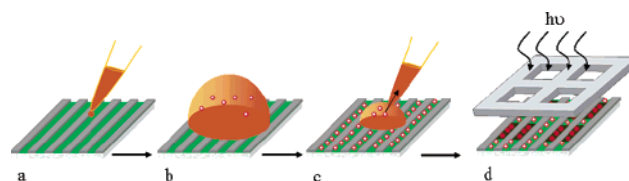


Figure 1. Schematic illustration of the procedure for the formation of hierarchical luminescent patterns. (a) Droplet of ~ 0.1 mg/mL solution of red-emitting CdSe NCs in 1-phenyloctane was dripped on a green-emitting self-assembled stripes. (b) CdSe NCs were selectively adsorbed on the pattern surface. (c) After 5 min, the droplet was removed by a pipet or a filter paper. (d) The obtained second level pattern was exposed to light through a shadow mask to generate the third-level hierarchical pattern.

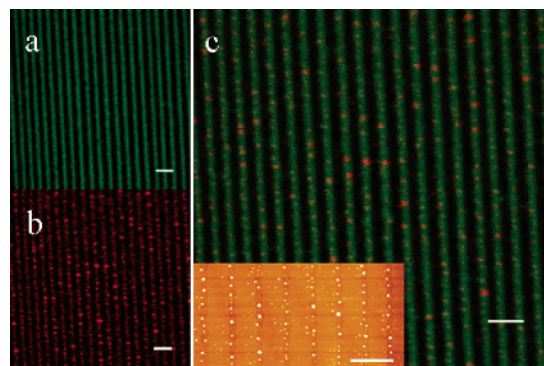


Figure 2. Lateral arrays of red-emitting CdSe NCs on the self-assembled pattern with green-emitting stripes. (a) CLSM image for BODIPY luminescent stripe patterns ($\lambda_{\text{ex}} = 488$ nm, detection range 500–550 nm). (b) CLSM image for CdSe NCs arrays ($\lambda_{\text{ex}} = 488$ nm, detection range 650–700 nm). (c) Merged image of images of a and b. (Inset) Corresponding AFM image (scale bar = 2 μm).

or a filter paper (Figure 1c). It was found that the red-emitting CdSe NCs accumulate in the green luminescent stripes, confirmed by microscopy measurements shown in Figure 2. Figure 2a shows self-assembled green stripes of luminescent BODIPY molecules ($\lambda_{\text{ex}} = 488$ nm, detection range 500–550 nm) imaged by confocal laser scanning microscopy (CLSM, Leica TCS SL, Heidelberg). Figure 2b shows the array patterns of red-emitting CdSe NCs ($\lambda_{\text{ex}} = 488$ nm, detection range 650–700 nm). Figure 2c, the merged image of a and b, shows the second level pattern we obtained. The strongly luminescent dots with the interparticle distance of 370 ± 60 nm are clearly identified within the channels by AFM measurement (Nanoscope IIIa, Dimension 3000, Santa Barbara, CA) shown in the inset to Figure 2c. This demonstrates that most of the NCs are deposited into the green-emitting stripes. It is known that the green stripes are formed by expanded DPPC enriched in BODIPY, while the dark stripes are mainly composed of condensed DPPC.¹⁷ The selective adsorption of CdSe NCs into the green-emitting stripes could be caused by the differences in wettability due to different

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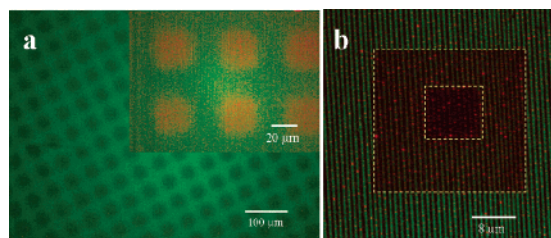


Figure 3. Hierarchical luminescence patterns. (a) Fluorescence images showing that the photoactivation of CdSe NCs and the photobleaching of BODIPY through a shadow mask reproduced the multiplexed luminescent pattern on CdSe/BODIPY layer. (b) CLSM image of the multiplex luminescence pattern due to different illumination time.

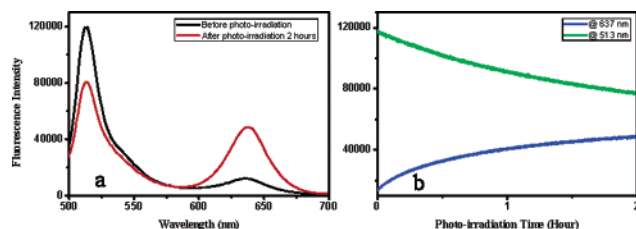


Figure 4. Changes in the luminescence intensity of CdSe NCs and BODIPY under continuous illumination. (a) Fluorescence spectra for CdSe NCs on self-assembled patterns before and after illumination. (b) Kinetic plots (the time evolution) demonstrating the photoactivation of luminescence for CdSe NCs and the photobleaching of BODIPY.

surface energies for 1-phenyloctane on expanded DPPC and condensed DPPC. The work of adhesion of 1-phenyloctane on expanded DPPC is 62.0 mJ/m², whereas the work of adhesion of 1-phenyloctane on condensed DPPC is only 53.7 mJ/m² (Supporting Information). The density of NC coverage is determined by the concentration of NC solution and the duration of exposure of NC solution to the patterned surface.¹⁹ The capillary force could be another factor to direct the assembly process of CdSe NCs.²⁰

Finally, the second-level pattern (lateral arrays of CdSe NCs on the self-assembled green-emitting stripes) is exposed to light through a shadow mask (500 mesh copper grid, square holes with side 28 nm) (Figure 1d) to obtain a hierarchical luminescence pattern (third level), demonstrated in Figure 3a. The areas exposed to the light (the squares) appear red. The green lines correspond to the regions shielded by the mask. We observed no morphology variations after the photoirradiation. The resolution of the third-level pattern is similar to the resolution of photolithography, i.e. limited by the diffraction of light.

Illumination of the samples with high-intensity light caused partial photobleaching of luminescent BODIPY molecules because of destruction of the fluorophore, whereas the luminescence of CdSe NCs increased. The mechanism of photoinduced fluorescence enhancement of CdSe NCs, which has been investigated under different conditions, has not yet been completely clarified.^{14–16} Exposure to light of the freshly made film for 2 h resulted in a significant decrease of intensity at 513 nm (the peak of the luminescence of BODIPY) and an enhancement of the intensity at 637 nm (the peak of the luminescence of CdSe NCs), as shown in fluorescence spectra of Figure 4a (ISA Jobin Yvon-SPEX FL3-22 spectrometer). The kinetic plots (Figure 4b) show clearly the photobleaching of BODIPY and fluorescence enhancement (increased 5 times after 2 h) of CdSe NCs. According to these properties, we have produced another kind of hierarchical lumi-

nescence pattern, as shown in Figure 3b, in which the different squares are exposed to light for different times. The exposure time for the inside square is longer than exposure time for the outside square; as a result, we can only observe red-dot arrays in the inside square, while there are orange dots on the green stripes in the outside square. Furthermore, due to the multiplicity of dyes and the tunability of the DPPC stripe pattern,²¹ one could expect to achieve multicolor patterns with an adjustable overall spectrum in different extended lengthscales.

In summary, we report a high-throughput procedure which allows us to generate hierarchical luminescence patterns based on multi-scaled self-assembly and specific properties of CdSe NCs and dyes in response to light irradiation. The procedure is remarkably controllable, high-yielding, and easy to implement. The ability to generate hierarchical luminescence patterning with relatively inexpensive instrumentation will facilitate the investigation of other self-assembled systems and should open up ways to fabricate novel advanced functional systems. In addition, adjusting the overall spectrum will allow the registration of single patterns. Since several applications as fluorescent labels of biomolecules have already been found for the semiconductor NCs, one would expect that the hierarchical luminescence patterns could be of practical importance for the integration and registration of sensitive sensor arrays.

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Supporting Information Available: A figure showing partial wetting of CdSe NCs droplet on the self-assembled pattern and the calculation of the work of adhesion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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