

Multicolor Luminescence Patterning by Photoactivation of Semiconductor Nanoparticle Films

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Production of user-defined 2D patterns of semiconductor nanoparticles (NPs) is a fundamental milestone for many photonic, biophotonic, and optoelectronic applications of quantum-confined species. For mesoscale patterns required for most currently used devices, the dominant approach to the problem involves spatially controlled chemical derivatization of the surface by affinity elements that subsequently bind NPs.¹ The pattern contrast in this case is limited by the selectivity of NP bonding, which is often smeared by strong and indiscriminate van der Waals attraction inherent for heavy and polarizable NP cores.² Patterning of NP surfaces can also be accomplished by photo- and stamp-lithography,³ taking advantage of the layer-by-layer assembling (LBL) strategy.⁴ The pattern contrast here is amplified due to the repetitive nature of the process and/or subsequent removal of the particle-negative areas.^{3a} The polymer-on-polymer stamping technique was used to make the patterns of organic luminescent materials comprising side-by-side red- and blue-emitting elements.⁵ Here, we demonstrate a new approach to functional patterning of multicolor optically active NP films, which combines some advantages of LBL as well as high-throughput and simplicity of photolithography. Instead of inducing morphological or chemical changes in the surface *prior* to the assembly of nanocolloids, the required optical properties, in our case, high quantum yield luminescence, are imparted to the films *after* the assembly as a result of photostimulated reactions on the NP surface. Importantly, the same technique may be used to produce not only monochrome but also multicolor images, similar to high-resolution SPM-produced patterns.⁶

Aqueous, citrate-stabilized CdSe/CdS core/shell nanocrystals with fluorescence maxima at 604, 576, and 534 nm, which were determined by the Cd-to-Se ratio (quantum yield, QY, ~0.5–2%), were synthesized as described in our previous publications.⁷ Exposure of freshly made CdSe or CdSe/CdS dispersions to ambient light for several days (intensity 0.12 mW) was noted to result in a drastic enhancement of the luminescence intensity with QY reaching as high as 25–45%, while no obvious increase in photoluminescence was observed for the same samples stored in the dark. Similar effects were also reported by several other groups with smaller changes in QY. It increased ca. 3 times for thioglycolic acid-capped CdTe nanocrystals illuminated for 5 days to become 30%.^{8a} Exposure of CdSe/CdS/ZnS nanorods to laser light overnight resulted in a QY increase of luminescence yield from 1 to 16%.^{8b} A 10% QY was obtained after UV curing ZnS:Mn samples coated with polymers.^{8c} For citrate-stabilized CdSe and CdSe/CdS colloids, the luminescence intensity of the excitonic peak typically increased 50–500 times both for liquid and for solid states (Figure 1). The transition from “dark state” to “bright state” for citrate-stabilized

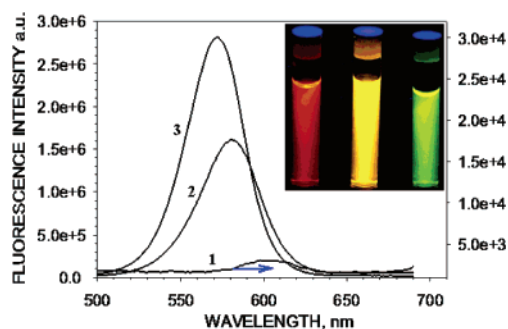


Figure 1. Emission spectra of CdSe/CdS (Cd:Se ratio = 4:1) core/shell nanoparticles measured after different irradiation times ($T = 298$ K, ambient light, aerobic environment): as made (1, right ordinate), exposed for 15 days (2), exposed for 25 days (3). Insert: evolution of luminescence color for CdSe/CdS citrate-stabilized colloids for extended light exposure.

NPs involves reaction(s) of NPs with ambient oxygen; its details are being investigated.⁹

The well-known process of NP photoetching accompanies the photoactivation, observed as a gradual blue shift of the luminescence peak for long exposure time (Figure 1). This process can be used to control the emission wavelength of NPs in addition to the original synthetic conditions. Concurrently, the illumination can also be performed in the solid state, where photoetching is decelerated and, therefore, partially decoupled from photoactivation. Solid matrix also affords spatially selective illumination. Taking into account the high contrast in luminescent intensity between dark and bright states of NPs and tunability of the particle diameters, we found that this system may provide a versatile platform for multicolor patterns, which we intended to demonstrate in this work.

Thin solid films of CdSe/CdS on glass slides and Si wafers were prepared by the standard LBL procedure with poly(diallyldimethylammonium chloride) (PDDA) (MW 400,000–500,000)¹⁰ (see Supporting Information). (PDDA/NP)₇ films (seven deposition cycles) were made from NPs in the dark state. 200-mesh TEM copper grids were placed on top of the film as lithography masks. Figure 2 shows a series of fluorescence microscopy images of thin films after 72 h of illumination by a 60 W table lamp in the dry state (intensity 4.7 mW). The highly luminescent squares are observed in the irradiated areas, while the dark lines correspond to nonirradiated regions shielded by the TEM grid. Pictures of different colors can be made by employing NPs of different diameters in the LBL deposition. The green, yellow, and red emissive patterns shown in Figure 2a–c correspond to multilayer films made from three different CdSe/CdS dispersions with original emission maxima at 604, 576, and 534 nm. The pattern dimensions, that is, $95 \pm 5 \mu\text{m}$ and $30 \pm 5 \mu\text{m}$ for the size of the square openings and the width of connecting bars, respectively, are in exact agreement with the grid specifications.¹¹ Topography images (Figure 2d) taken in

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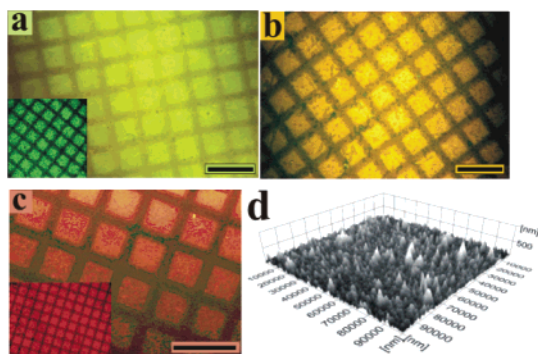


Figure 2. (a–c) Fluorescence and confocal (inserts) microscopy images of light-induced 200-mesh grid patterns made for NPs of different diameters. (d) Topography image of the patterned film (Nanostation, courtesy of Accurion). Scale bar 200 μm . To avoid possible water vapor condensation around the grids, they were immersed in a dodecanethiol/toluene solution for 1 day.

ten spots indicate that the observed patterns are exclusively optical: there are no apparent height variations correlating with the grid geometry.

The luminescence contrast obtained by photoactivated patterns is comparable to or better than NP patterns obtained before.^{2,3,5} Two important points need to be made considering the pattern resolution and sharpness. (1) Physical dimensions of optical inhomogeneities correlate well with the size of topographic features (Figure 2d). This indicates that some of them (Figure 2b) should be attributed to surface roughness and local variation of illumination conditions. Additionally, dust particles are often included in the multilayers when the LBL deposition is performed at ambient conditions. Provided that these issues are resolved, the combination of high homogeneity of LBL nanocomposites¹² and near-field optics makes possible nanometer-scale luminescence patterns. (2) Because the rate of photoactivation of the CdSe/CdS citrate-stabilized NPs was insignificant without oxygen, the obtained luminescence patterns may be fixed from fading under light by coating the film with, for instance, O₂-blocking transparent sol–gels.¹³ Without any special coating, the prepared patterns retained the contrast for several months when stored in the dark.

If the LBL film remains exposed to light and air, one can observe the evolution of colors similar to that in Figure 1. Thus, it appears to be possible to obtain multicolor NP patterns using light as the only drawing tool. This will avoid multiple processing steps and circumvent the problems of indiscriminate NP adsorption. The proof-of-concept demonstration of the multicolor patterning with light was carried out on a (PDDA/NP)₁₀ film made from CdSe/CdS deposited in the dark state on glass slide. After activation, the NP film acquired distinct orange-red luminescence at 585 nm (Figure 3a). One-half of the slide was then masked and irradiated for 12 more days (intensity 4.6 mW, Figure 3b). The luminescence of the uncovered part of the film turned green due to photoetching (470–520 nm), while the emission of the covered part remained orange (575 nm). A slight blue shift of the luminescence in the covered part is due to waveguiding of light in the glass slide from the exposed part to the masked part.

The presented optical patterning technique does not require chemical functionalization of the surfaces and subsequent processing as in standard photolithography or conventional photography. Moreover, as compared to topographic, reflective, or absorptive images, luminescence patterns provide the highest signal-to-noise ratio and, therefore, are preferential for optical devices, information

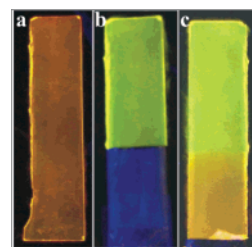


Figure 3. Optical image of the (PDDA/NP)₁₀ film (a) after initial activation and after photoetching with (b) and without (c) the mask (Al foil). Two different emission colors are clearly visible in the slide (c). All pictures were taken under black light illumination.

processing, and biophotonics. For all of these areas, multicolor capabilities associated with quantum-sized effects of semiconductor NPs including 2D color drawing enable new processing approaches and device functions. Optimization of the presented patterning approach should include the acceleration of photoactivation and finer control over spatial and spectral resolution of emitted light. Stratified layered composites¹⁴ providing a versatile platform for structural alterations should simplify this task. The most immediate potential applications of this patterning format are envisioned in cryptography and cell tagging. As such, patterns from a photoactivatable mutant of the green fluorescent protein were recently used for in vivo studies of intracellular protein dynamics.¹⁵ Simplicity of the synthesis of citrate-stabilized CdSe/CdS NPs, tunability, and high intensity of their emission provide important advantages over the recombinant fluorescent proteins.

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Supporting Information Available: The layer-by-layer assembly of CdSe/CdS citrate-stabilized NPs exhibits typical linear behavior: the average thickness of the adsorbed film increases linearly with the number of deposition cycles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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