DNA-Based Nanotechnology: Highly Luminescent CdSe – DNA Nanoscale – Engineered Complexes

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ABSTRACT

We present some new results within the concept of biopattern nanoengineering - including using DNA molecules as building blocks and nanotemplates for controllable fabrication of various bioinorganic nanostructures due to their unique physical-chemical properties and recognition capabilities and the synthetic availability of desired nucleotide sequences and length. We have synthesized novel DNA complexes with positively charged, highly luminescent CdSe nanorods that can be self-organized into filamentary, netlike, or spheroidal nanostructures. DNA-CdSe-nanorod filaments possess strongly linearly polarized photoluminescence due to the unidirectional orientation of nanorods along the filaments. Within activities of INTC of Russia (INTC – Interdisciplinary Nanotechnology Consortium) we have developed the complete technological cycle of design, manufacturing, characterization and application of molecular nanoclusters (MNC) for nanoelectronics and some other areas.

Keywords: nanoengineering, DNA, nanorod, semiconductor, photoluminescence.

We present some new results within the concept of using DNA molecules as building blocks and nanotemplates for controllable fabrication of various bioinorganic nanostructures due to their unique physical-chemical properties and recognition capabilities and the synthetic availability of desired nucleotide sequences and length. Development of new effective nanofabrication methods with reasonable costs is currently of principal importance for practical advancements in nanoscience and nanotechnology. Within activities of INTC of Russia (INTC – Interdisciplinary Nanotechnology Consortium) we have developed the complete technological cycle of design, manufacturing, characterization and application of molecular nanoclusters (MNC) for nanoelectronics and some other areas. We have also synthesized novel DNA complexes with positively charged, highly luminescent CdSe nanorods that can self-organize into filamentary, netlike (Fig 1.), or spheroidal nanostructures. DNA-CdSe-nanorods filaments possess strongly linearly polarized photoluminescence due to the unidirectional orientation of nanorods along the filaments (Fig 2.) [1-3].

Unlike spherical nanoparticles, elongated and rod-shaped direct-band semiconductor nanocrystals, such as CdSe nanorods, possess a unique optical property: their photoemission is highly polarized along the longer axis, even at room temperature. That makes them useful nanoscale building blocks for development of microemitters of polarized light and micron-scale polarization sensitive photosensors. To achieve this goal, a cost-effective technology must be developed that allows for the controllable fabrication of nanostructures with nanorods both arranged in the right place and with the appropriate orientation. Such technology can be based on either self-assembling or nanotemplate-directed deposition. Recently, we have demonstrated how specially prepared single semiconductor nanowells may be utilized for unidirectional electrostatic deposition of CdSe nanorods in a single line.4 The restricted geometry of the well along the transverse direction (the width of the nanowell is less than the nanorod diameter) leads to the orientation of nanorods along the well. The utilization of nanowell nanotemplates requires a high-quality technique for homogeneous thin film deposition that may be difficult to achieve in a large-scale production. Alternatively, natural materials like widely used DNA molecules may be exploited as another type of

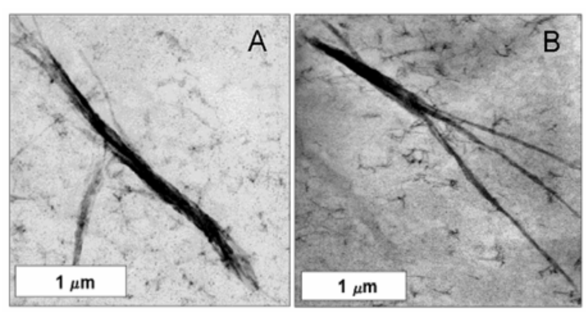

Fig. 1. TEM images of self-organized filamentary complexes of DNA with cationic CdSe nanorods obtained by long (5 min) incubation of DNA-PVPy-20 LB films in the aqueous colloidal solution of cationic CdSe nanorod. The image 2b demonstrates the bunchlike character of DNA-CdSe nanorod filamentary aggregates.

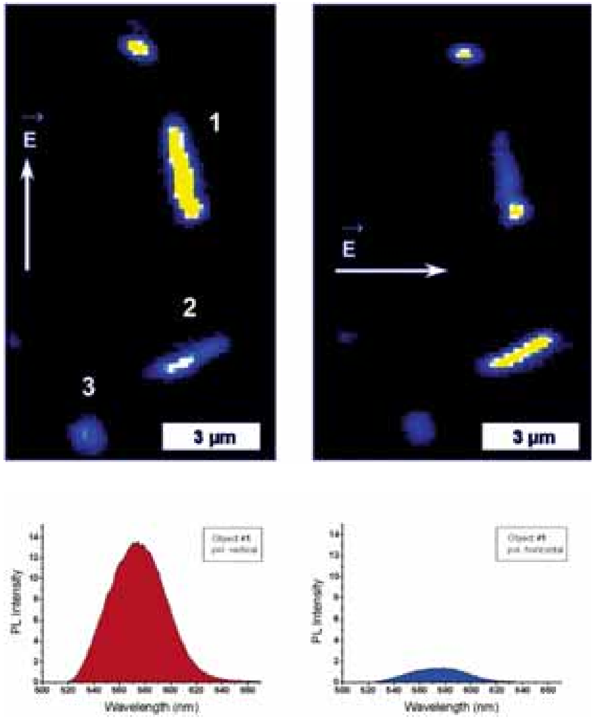

Fig. 2. Room-temperature polarized micro-PL images of DNA-CdSe nanorod complexes. The images were obtained using a home-built optical setup including a cw Ar ion laser as the excitation source (λ) 488 nm, 50 mW, a Zeiss Achromate objective, 20, NA 0.4, a CCD video camera, and a high-resolution imaging monochromator equipped with a CCD camera. The collected light was filtered through a 2 mm orange filter placed just after the objective in order to remove completely the scattered laser light. The rotating linear polarization filter was placed behind the orange filter. The polarization is vertical on the left image and horizontal on the right one. Both images are represented in false-color scale with PL intensities increased from black through blue to yellow. At the bottom, the corresponding room-temperature PL spectrum of the object 1 confirms the strong polarization of emission along the filament (the red spectrum is for vertical polarization, the blue one for horizontal).

inexpensive nanotemplate and scaffolds for controllable deposition and orientation of nanorods. We call this approach boipattern nanoengineering. Previously, DNA was utilized as a nanotemplate for nanowire-like deposition of gold and silver colloids, semiconductor quantum dots, and selective metallization. Here, we report on the new nanoscale-organized bioinorganic nanostructures formed by cationic (positively charged) highly luminescent CdSe nanorods and anionic DNA molecules. These molecules were initially organized into planar aggregates on the flat substrate surface by complexation with amphiphilic polycation. Surprisingly, the electrostatic interaction between CdSe nanorods and planar DNA complexes gives rise to selforganized nanostructures in which DNA-CdSe nanorod complexes are arranged into collinear strings or filaments of micrometer length.

It is important to know how CdSe nanorods are arranged in their filamentary complexes with DNA. To distinguish between random orientation and unidirectional alignment along the filaments, we utilized the ability of our CdSe nanorods to emit strongly linearly polarized light in the well-defined spectral region. The silicon substrate with DNA-nanorod complexes was illuminated by laser light and the PL emission from highly luminescent CdSe nanorods was collected by a microscope objective, passed through a rotating polarization filter, and registered using a CCD video camera. Figure 2. shows polarized micro-PL images of DNA-CdSe nanorod complexes. Without the polarizer, the PL images show the presence of a large amount of bright filaments with the length varied somewhat between 1 and 5 µm. The diameter of these filaments cannot be determined precisely from the PL image and is rather below the optical resolution of our setup, i.e., < 0.5 µm. The room-temperature PL spectra of these filaments possess a narrow nearly symmetrical band centered at ca. 580 nm. No noticeable PL emission from bare DNA molecules or DNA-PVPy-20 complexes was observed in our experiments, which means that the PL image of the filaments was formed by highly luminescent CdSe nanorods.

In conclusion, we demonstrate here the formation of selforganized complexes of positively charged highly luminescent CdSe nanorod and DNA molecules. A variety of different forms of self-organized DNA-nanorod complexes makes the proposed method potentially useful for nanofabrication of new hybrid bioinorganic nanostructures with advanced structure and optical properties.

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