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Self-Organized, Highly Luminescent CdSe Nanorod−DNA Complexes

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Abstract: DNA molecules are useful 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.

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.[1] That makes them useful nanoscale building blocks for development of microemitters of polarized light and micron-scale polarization sensitive photosensors.[2] 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[3] 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 inexpensive nanotemplate and scaffolds for controllable deposition and orientation of nanorods. Previously, DNA was utilized as a nanotemplate for nanowire-like deposition of gold and silver colloids,[5,6] semiconductor quantum dots,[7] and selective metallization.[8]

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 self-organized nanostructures in which DNA−CdSe nanorod complexes are arranged into collinear strings or filaments of micrometer length.

CdSe/ZnS core−shell nanorods 22 nm in length and 4.5 nm in diameter were chemically synthesized according to the modified procedures described in ref 9 (the details of ZnS shell growth are described in the Supporting Information). The room temperature photoluminescence (PL) band is centered around 580 nm with PL quantum yield above 30% at room temperature (in the chloroform solution). The nanocrystals were positively charged and solubilized in water using the surface exchange of organic hydrophobic shell (trioctylphosphine oxide) onto hydrophilic positively charged dimethylaminoethanethiol hydrochloride (DMAET).

Planar complexes of DNA and amphiphilic polycation on the solid substrate were obtained first, by the formation of a Langmuir monolayer of water-insoluble amphiphilic cationic derivative of poly(4-vinylpyridine) with 20% of the cetylpyridinium groups (PVPy-20) at the air−water interface. Then, DNA molecules from the aqueous phase bound with amphiphilic

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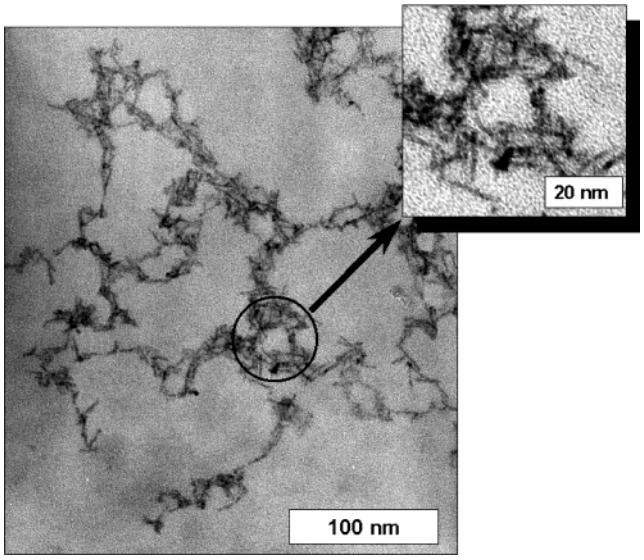

Figure 1. TEM images of CdSe nanorods deposited on planar DNA−PVPy-20 complex by short (1 min) incubation of DNA−PVPy-20 LB film in the aqueous colloidal solution of cationic nanorods. The inset shows a part of the original image with higher magnification in order to resolve the single isolated nanorods. TEM images were obtained at room temperature with a JEOL JEM-100B microscope.

polycation monolayer to form the DNA−PVPy-20 complex. The DNA−PVPy-20 Langmuir−Blodgett films were transferred on the surface of Si wafers and Formvar-coated TEM copper grids.[10] A DNA−PVPy-20 LB film was used as template for fabrication of DNA−CdSe nanorod complexes via electrostatic interaction between cationic nanorods and negatively charged DNA side phosphate groups. DNA−CdSe nanorod complexes were formed by incubation of supported DNA−PVPy-20 LB films in the aqueous colloidal solution of cationic CdSe nanorods. The substrates with immobilized complexes were rinsed with pure water before and after incubation in order to remove free and weakly bound nanorods or DNA molecules.

Figure 1 shows DNA−PVPy-20 film after short (<1 min) incubation in the aqueous solution of cationic CdSe nanorods. Since DNA itself is nearly transparent to the electron beam, the TEM image is constructed by the nanorods bound to the DNA chains. The higher magnification image in the inset shows individual isolated nanorods ca. 4 × 20 nm in size. Most of the nanorods were oriented rather randomly, while some of them certainly arranged along the DNA chain (see, for example, the bottom left quarter of Figure 1). The morphology of DNA−nanorod complexes in Figure 1 is very similar to the extended netlike and quasicircular toroidal structures of the planar DNA−amphiphilic polycation complexes observed earlier.[10,11]

Hence, the short incubation time of DNA−PVPy-20 complex in the nanorods solution results in a simple decoration of DNA chains with CdSe nanorods. The nanorods themselves in this case do not affect substantially the morphology of DNA molecules in the initial DNA−PVPy-20 complexes.

Surprisingly, longer incubation time gives completely different results. Figure 2a demonstrates the TEM image of DNA−PVPy-20 film after 5 min of incubation in the nanorods solution.

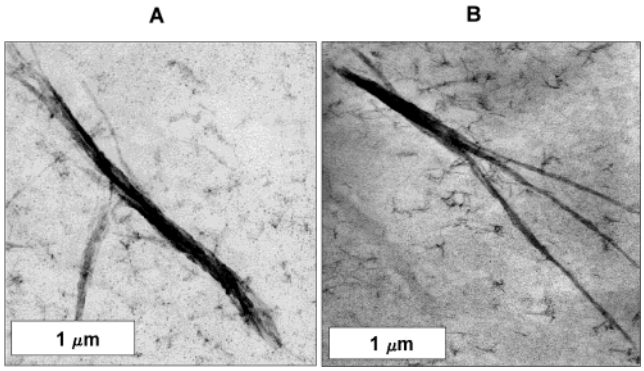

Figure 2. TEM images of self-organized filamentary complexes of DNA with cationic CdSe nanorods obtained by long (5 min) incubation of DNA−PVPy-20 LB films in the aqueous colloidal solution of cationic CdSe nanorod. The image 2b demonstrates the bunchlike character of DNA−CdSe nanorod filamentary aggregates.

The resultant DNA−CdSe nanorods or mixed DNA−PVPy-20−CdSe nanorod complexes form organized highly anisotropic linear structures. Such filaments can exceed 1 μm in length and their diameter is around 100 nm or less. In Figure 2b the complex structure of DNA−nanorods filament is seen clearly: the filament consists of a number of much thinner plaits. Some plaits carrying only solitary collinearly arranged CdSe nanorods are formed by single DNA molecules. The control experiments made with DNA and nanorod-free solutions did not give any type of organized anisotropic structures. This means that the specific electrostatic interaction between cationic nanorods and DNA−polycation complexes is a driving force in the self-organization of DNA−nanorod structures into ordered filamentary complexes. Yet the detailed mechanism of this process is not clear, but we suppose that cationic nanorods substitute for the polycation molecules in the DNA−PVPy-20 complex and the anisotropic uniaxial geometry of nanorods provokes DNA−nanorod complexes to combine into linear filaments. Generally, the architecture of DNA−nanorod complexes may be even more diverse and will be discussed below.

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 3 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.

Also, a control experiment with bare substrate (no DNA) treated in the nanorods solution revealed the absence of

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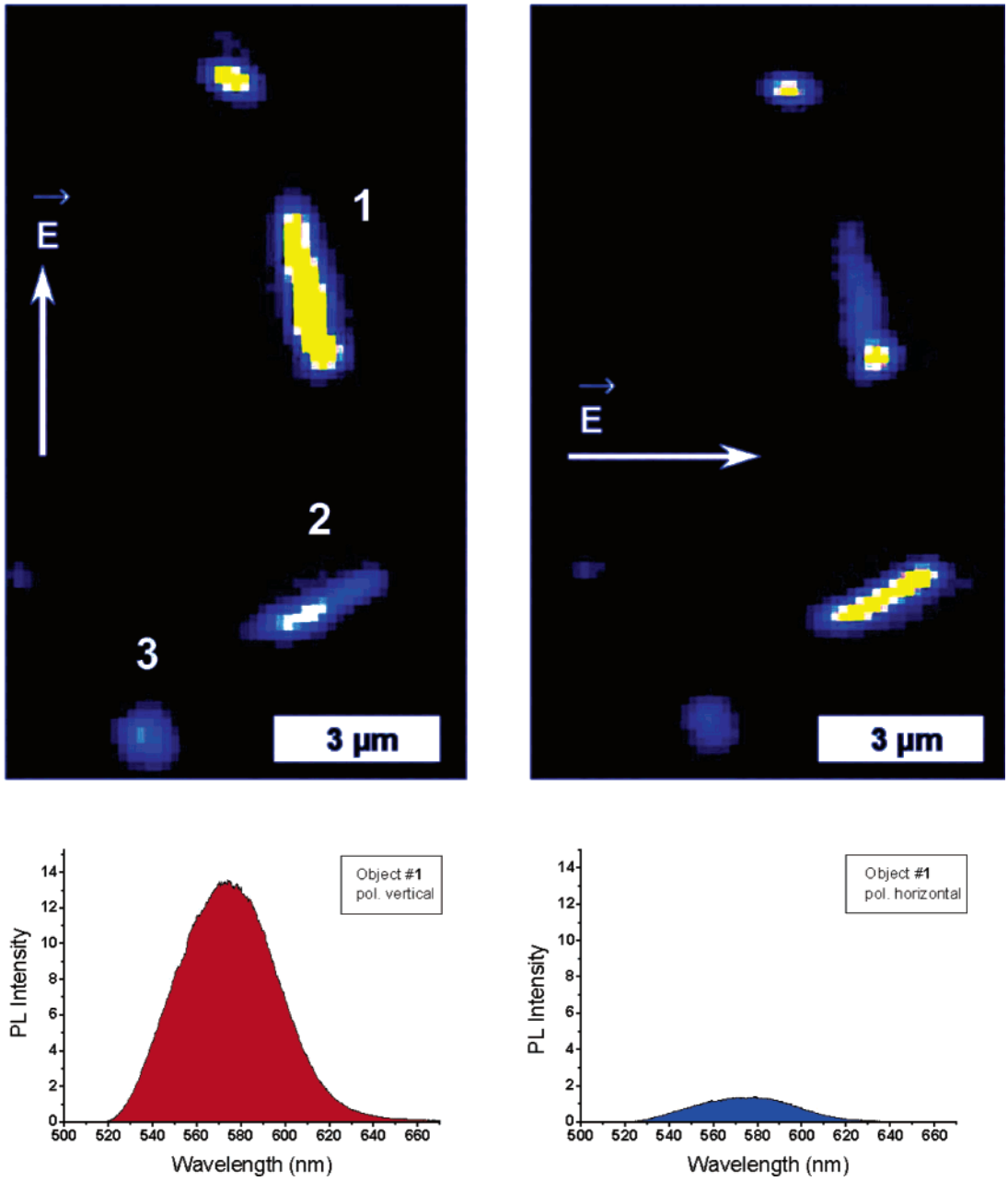

Figure 3. Room-temperature polarized micro-PL images of DNA−CdSe nanorod complexes. The images were obtained using a home-built optical setup including a cw Ar ion laser as the excitation source (λ = 488 nm, 50 mW), a Zeiss Achromate objective, ×20, NA = 0.4, a CCD video camera, and a high-resolution 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).

noticeable PL background from nonselectively bound nanorods. Hence, we conclude that the bright filaments in PL images are due to the isolated micron-sized DNA−CdSe nanorod complexes. By rotating the polarization filter by 90° we registered the sets of pairs of PL images with light polarized in either vertical or horisontal direction. In Figure 3 we show a pair of nearly orthogonally oriented filaments 1 and 2. It is clearly seen that the PL image of 1 is brightest when the light is polarized vertically, while 2 is brightest under horizontal polarization. At the bottom left we see also a polarization-insensitive image of nearly circular object 3, perhaps another type of DNA−CdSe complex with nanorods oriented isotropically relative to the polarization filter. To qualitatively confirm the strongly polarized PL image of DNA−nanorods filaments we have measured the PL spectra of object 1 using a double monochromator equipped with a CCD camera. The spectra are shown at the bottom of Figure 3 and show that the PL signal from object 1 is nearly 10 times larger when the polarizer is oriented vertically along the DNA−nanorod filament. The observed highly polarized nanorod emission in Figure 3 allows one to conclude that the filaments indeed contain a large amount of CdSe nanorods oriented mostly unidirectionally along the filaments.

It seems likely that the process of self-organization of DNA−nanorod complexes develops in time relatively slowly and

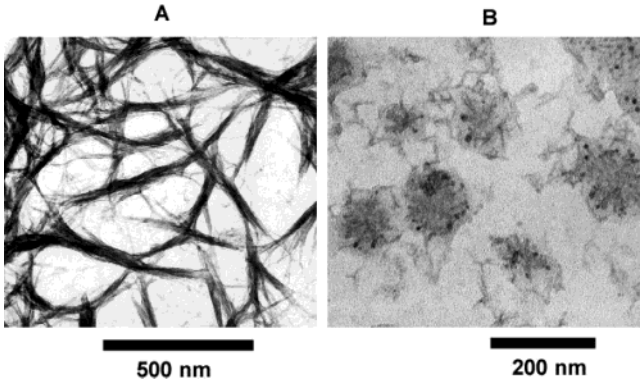

Figure 4. (A) TEM image of DNA−nanorod netlike superstructure formed by prolonged incubation (about 7 min) of supported DNA−PVPy-20 LB films in the cationic CdSe nanorod solution. (B) TEM image of the circular DNA−nanorod structures.

involves a progressive substitution of cationic PVPy-20 quaternary ammonium groups by positively charged nanorods carrying similar cationic groups. At much longer incubation times red flakes appear in the solution, which means that at the late substitution stage the DNA−nanorod complexes completely lose bonds with water-insoluble PVPy film on the substrate and leave for water solution. Depending on the structure of the initial DNA−amphiphilic polyelectrolyte complex (nets, toroids[10]) the *crystallization* of DNA−nanorods may proceed by different ways. Figure 4a shows the DNA−nanorod complex superstructure obtained via prolonged incubation (about 7 min) of supported DNA−PVPy-20 complexes in the nanorod solution. This netlike structure may result from progressive intergrowth and interpenetration of filaments with the formation of a hierarchically organized architecture of DNA−nanorod complexes.

In Figure 4b we also demonstrate the circular DNA−nanorod structures that are probably responsible for isotropically polarized circular object 3 in the micro-PL image in Figure 3.

In conclusion, we demonstrate here the formation of self-organized 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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Supporting Information Available: Details of the preparation of CdSe/ZnS core−shell nanorods, water-soluble CdSe nanorods, and DNA−polycation complexes are described. This material is available free of charge via the Internet at http://pubs.acs.org.

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