Unidirectional Alignment of CdSe Nanorods

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ABSTRACT

Cadmium selenide nanorods, unique nanostructures which possess bright and up to 100% polarized photoluminescence, now can be arranged unidirectionally in a single line. The method is based on the chemical attachment of nanorods to the surface of a single cleaved semiconductor nanolayer and exploits a combination of wet-chemical and epitaxial growth techniques to produce templated semiconductor nanostructures. The nanotemplate here is a ZnS layer with a thickness less than the diameter of the nanorods. Binding the nanorods to the template, the limited space provokes an enhanced alignment of the rods along the ZnS layer which can be proved by the high polarization degree of the nanorods emission.

A “bottom-up” approach in nanotechnology requires well-defined nanoelements to be placed on well-defined positions. II−VI semiconductor nanocrystals may be suitable nanoelements for both nanoelectronic and nanooptical devices due to discrete energy levels controlled by the size of the nanocrystals.1 Recently, CdSe nanocrystals have been proposed as working elements for nanotransistors,2 electrochromic materials,3 and charge-coupling devices.4 The chemical synthesis of high-quality CdSe, CdTe, ZnSe, etc. nanocrystals is now becoming a routine procedure.5 In contrast, the well-controlled one-dimensional arrangement of nanocrystals into electronic circuits, or nanooptical elements, yet is still a “state-of-the-art” problem. Based on electrostatic or chemical attachment, the nanoarrangement of nanocrystals first requires the preparation of a suitable nanotemplate. Recently, charged polymeric chains (polyelectrolytes)6 or single-walled carbon nanotubes7 have been used, as such templates for attachment of highly luminescent CdSe nanocrystals. An important problem is to control precisely either the position of the nanocrystals or their orientation. The latter, while being not essential for spherical nanocrystals, can be very important for nanorods. Synthesized for the first time only few years ago, CdSe nanorods8 came to be exciting materials due to some important properties: up to 100% polarized luminescence.9 Linearily arranged highly luminescent CdSe nanocrystals could be utilized as nanoemitters or high-resolution detectors of polarized light (recently, this idea was demonstrated on InP rods10). To the author’s knowledge there was only one attempt to control the orientation of CdSe nanorods in the liquid crystals regime;11 instead most applications require solid-state materials. In this paper we propose the utilization of a single semiconductor nanolayer as an intrinsic template for linear arrangement of CdSe nanorods.

We prepared a single ZnS nanolayer grown on BaF2 substrate and covered by a SiO2 cap layer. First, a 5 nm thickness ZnS layer was vacuum evaporated onto a single-crystal BaF2 10 × 10 × 1 mm3 substrate. Then, a 100 nm SiO2 layer was deposited in the same vacuum chamber atop the ZnS layer. Finally, we cleaved the sample orthogonally to the surface plane (single-crystal BaF2 is a highly brittle material) which opened a single 5 nm ZnS stripe at the edge (Figure 1a). This ZnS stripe is suitable for further highly spatially localized attachment of CdSe nanorods (as well as CdSe nanodots, if required). This technique is similar to the cleaved-edge overgrowth in molecular beam epitaxy to produce semiconductor nanowires. Because ZnS is a wide-gap semiconductor and nonabsorbing material in the region of nanorods emission, we assume the absence of possible energy transfer, or sufficient charge injection from nanorods to ZnS nanotemplate which could complicate the phenomenon.

(CdSe)ZnS core−shell nanorods 35 nm in length and 7 nm in diameter (Figure 1b) were synthesized according to known procedures developed in refs 12 and 13. Nanorods possess a photoluminescence (PL) band centered around 670 nm, and nearly 80% polarized PL emission at room temperature (tested in a single rod experiment). The spectral line width of the PL band is about 45 nm (95 meV) at room

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Also, for the reference experiment we synthesized the usual (CdSe)ZnS core–shell quantum dots of 5 nm in diameter with no significant PL polarization at room temperature. The chemical attachment of both CdSe nanorods and nanodots to the ZnS stripe was achieved by using hexanediethiol. A prolonged treatment of the cleaved BaF₂/ZnS/SiO₂ sample in 1% solution of hexanediethiol in 2-propanol resulted in formation of a self-assembled monolayer (SAM) of dithiol only on the ZnS stripe via reaction between one dithiol –SH groups and surface zinc atoms. Both BaF₂ and SiO₂ do not react with dithiols. The formation of a close-packed SAM of various thiols and dithiols on the surface of noble metals, II–VI, III–V semiconductors, etc., is well-known (see, for example 14 and references therein). In our case, second dithiol –SH groups remain available for chemical attachment of CdSe nanorods. The attachment of nanorods was done by the prolonged treatment of the sample in a colloidal solution of nanorods in chloroform. The main goal of the experiment was to examine whether the ultranarrow ZnS/SAM stripe with a width less than the diameter of the CdSe nanorods (ca. 5 nm versus 7 nm) and semi-infinite length would provoke the unidirectional attachment of rods along the ZnS/SAM nanotemplate. To verify this we utilized polarization-dependent PL imaging and spectroscopy of our sample. The sample was mounted with the cut edge vertical and facing the microscope objective (Zeiss Achromat ×65, NA = 0.95). The sample was illuminated by a 488 nm argon-ion laser and the emission was collected by the objective, passed through a cut-filter and pinhole either to CCD-video camera or a spectrometer equipped with a cooled CCD camera. A polarization filter was mounted in the detection beam path just after the pinhole. The orientation of the polarizer E can be varied between complete parallel and perpendicular orientation with respect to the main axis d of the ZnS stripe. All optical experiments have been done at room temperature.

Figure 1. (a) Sketch of sample consisting of single 5 nm wide ZnS nanolayer sandwiched between BaF₂ substrate and 100 nm SiO₂ film. The sample was cleaved in order to expose a 5 nm wide ZnS stripe to which CdSe nanorods (nanodots) are attached via hexanediethiol self-assembled monolayer. (b) TEM image of CdSe nanorods used to attach to the ZnS nanotemplate.

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Figure 2 shows the color-coded intensity maps and PL spectra of CdSe nanorods (left panel) and nanodots (right panel) attached to a single ZnS nanotemplate for different orientation of polarizer E in the optical pathway before detection: parallel to the ZnS stripe direction d, E // d, and orthogonal E ⊥ d. The excitation source is an Ar-ion laser (λ = 488 nm, 35 mW) focused to a ca. 50 micrometer diameter spot. The polarization of the laser beam always is parallel to d. (top) PL spectra for nanorods and nanodots. Both E // d and E ⊥ d PL spectra were recorded for the spots selected by a 50 μm pinhole and indicated by arrows in corresponding panels. Black PL spectra correspond to E // d, while red ones to E ⊥ d.

2 (left) clearly demonstrate that PL emission from CdSe nanorods attached to a ZnS/SAM stripe is strongly linearly polarized along the ZnS nanolayer template. Based on the knowledge of polarization of PL emission of single CdSe nanorods (i.e., ~90% single-rod linear polarization degree at room temperature), this result indicates a preferentially unidirectional alignment of nanorods along the ZnS stripe. Most of the bright spots in the color-coded map in Figure 2 (left frame) show pronounced blinking in time, which is indicative of single nanocrystal emission. The corresponding experiment for CdSe nanodots is shown on the right part of Figure 2. While for nanorods a strong intensity modulation is observed when turning the polarizer, the change in PL intensity is negligible for nanodots attached in an equivalent manner to the rods. The small difference between the $E_{\parallel}$ and $E_{\perp}$ PL spectra for the nanodots is caused by a slight deviation in the spectral sensitivity of the spectrometer for the two polarizations. The absence of polarized PL from the reference sample with nanodots eliminates possible optical artifacts since CdSe dots themselves possess no PL polarization.

To further support our hypothesis, we have modeled the variation in the polarization degree of an ensemble of nanocrystals starting from randomly aligned CdSe nanorods toward ordering in the nanorod axis orientation. The transition from nanodots to nanorods is simulated by changing the degree of linear polarization of the single nanocrystals from 0% (e.g., nanodots, weakly polarized emission) to 100% (ideal nanorods, completely polarized). Assuming equal polarization selection rules for both the emission and absorption processes and using a simple geometrical model, we calculated the intensity ratio between the PL-signal detected cross-polarized ($I_\perp$) and copolarized ($I_\parallel$) with respect to the excitation. By directional averaging of the ensemble emission, one can specify the maximum modulation of the detected intensity for random orientation in the nanocrystal axes (Figure 3). Unpolarized emitters (degree of linear polarization is zero in the $y$-axis of Figure 3) show simply no intensity modulation, i.e., the detected PL intensity stays constant at 100% of its maximum value (normalized to 1.0 in the $x$-axis of Figure 3) independent of polarizer orientations. For a 2D ensemble, the PL intensity is increasingly modulated with increasing degree of linear polarization of the light-emitting species, reaching the maximum possible modulation of $2\pi \approx 64\%$ for completely polarized emitters. It can be clearly seen that an ensemble of nanorods with randomly distributed axes will never show an intensity modulation that is below this ratio between $I_\parallel$ and $I_\perp$. The inset shows the experimental proof for a 2D ensemble of randomly oriented CdSe nanorods on glass, with $I_\parallel/I_\perp$ varying only between 0.7 and 1.0. Embedding the nanorod ensemble in a matrix-like polymer, the dielectric screening effects even further decrease the modulation between $I_\parallel$ and $I_\perp$ and the minimum ratio $I_\parallel/I_\perp$ rises up to 0.75. However, any ordering in the rod axis orientations is then immediately indicated by a value of $I_\parallel/I_\perp$ below 0.64. If the measured degree of polarization goes below this limit, it means the preferential alignment of CdSe nanorods in one direction. The calculated ratio $I_\parallel/I_\perp$ for the PL polarization shown in Figure 2 gives the value $\approx 0.3$, which is an additional indication on the efficient unidirectional alignment of CdSe nanorods.

In conclusion, the observation of highly polarized emission of CdSe nanorods deposited on a nanotemplate with a layer thickness smaller than the nanorod diameter and the absence of that effect for nanodots demonstrates the possibility of a unidirectional alignment of single CdSe nanorods on a ZnS nanotemplate. A further extension of this technique for the alignment of nanocrystals we see in the creation of much more complex structures such as multiple parallel nanotemplates, branched and crossed layers with nanorods and nanodots attached, which could be done by utilizing various microlithographic techniques. In particular, we propose to utilize a structure with two parallel ZnS stripes separated by controlled distances for a study of the Förster energy transfer between two lines of oriented nanorods.

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