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Nanotechnology **19** (2008) 215606 (8pp)

Domain and network aggregation of CdTe quantum rods within Langmuir–Blodgett monolayers

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Received 1 February 2008, in final form 10 March 2008 Published 21 April 2008 Online at stacks.iop.org/Nano/19/215606

Abstract

Control over the organization of quantum rods was demonstrated by changing the surface area at the air–liquid interface by means of the Langmuir–Blodgett (LB) technique. The LB isotherm of CdTe quantum rods capped with a mixture of alkylphosphines shows a transition point in the liquid–solid state, which is caused by the inter-rod reorganization. As we observed, at low surface pressure the quantum rods are assembled into round-shaped aggregates composed of a monolayer of nanorods packed in limited-size clusters with random orientation. The increase of the surface pressure leads to the rearrangement of these aggregates into elongated bundles composed of uniformly oriented nanorod clusters. Further compression results in denser packing of nanorods aggregates and in the transformation of monolayered domains into a continuous network of locally ordered quantum rods.

1. Introduction

Semiconductor nanocrystals are attractive nanomaterials because of their unique optical properties: extended absorption in the UV-visible region, a narrow and intense emission band, high brightness and photostability, and size-tunable optical emission in different regions including the nearinfrared [1-8]. Advanced colloidal syntheses enable the controlled preparation of monodisperse nanocrystals with band gap energy that is tunable due to the quantum confinement effect [9]. CdSe and CdTe nanocrystals are the most attractive for prospective applications because of their broad and tunable absorption and emission properties in solution as compared with other semiconductor nanocrystals. Therefore, these semiconductor nanocrystals have been proposed as prospective working elements for nanotransistors [10], electrochromic materials [11], and charge-coupling devices [12].

The possibility to manipulate the shape of nanocrystals has led to the synthesis of more complicated shapes beyond

traditional spherical quantum dots. Rod-shaped semiconductor nanocrystals have been prepared, hereafter referred to as 'quantum rods' [13]. Existing quantum rods are semiconductor nanocrystals with diameters ranging from 2 to 10 nm and length ranging from 5 to 100 nm, with typical aspect ratio in the range 2-5. In addition to the properties inherited from spherical nanocrystals (quantum dots), such as sizetunable broad absorption, narrow symmetric emission, and extreme resistance to photobleaching, quantum rods have larger absorption cross section [14] and faster radiative decay rate [15], and they can be functionalized with multiple binding moieties. Furthermore, a single nanorod exhibits linearly polarized emission unlike the plane-polarized light from a single quantum dot [13]. Moreover, the emission of a single quantum rod can be reversibly switched on-off by an external electric field [16].

Ordered assemblies of quantum rods on a surface have potential for use in optoelectronics, photonics, and biosensing, because their optical and optoelectronic properties can be different from those in a solution. The possibility of local ordering could result in nanomaterials with anisotropic optical

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properties [17]. Spontaneous self-assembly of quantum rods (CdS, CdSe, CdTe) during evaporation of solvent has been extensively studied in the last decade. CdSe and CdS quantum rods have been observed to collectively assemble into liquid-crystal phases under certain conditions [18-20]. For example, it has been observed that a nematic liquidcrystalline phase of these quantum rods formed prior to complete solvent evaporation [20]. When deposited from slowly evaporating solutions, superlattices can form with the quantum rods perpendicular to the surface of the substrate, and these serve as building blocks for three-dimensional (3D) solids with a choice of glassy, nematic, smectic or crystalline order [19]. Such superlattices can become larger in the presence of a global electric field [21-23], Russell and coworkers recently demonstrated various configurations of CdSe nanorod packing at a water-oil interface after evaporation of a solvent droplet [24].

In other studies, CdS quantum rods were reported to assemble head-to-tail into long stripe patterns [25], indicative of dipole interactions. The spontaneous organization of single CdSe quantum rods into tracks over 1 μ m in length was also observed [26]. Recently, highly ordered concentric rings consisting of CdTe quantum rods have been produced by allowing a drop to evaporate from a sphere-on-flat Alivisatos *et al* have prepared materials geometry [27]. for solar cells on the base of conjugated polymer poly(3hexylthiophene) (P3HT) and CdSe rods [28]. Incorporation of quantum rods into conjugated polymer increased the charge transfer rate and extended the absorption spectrum up to 700 nm, which allowed a significant increase in the power conversion efficiency compared to existing polymeric-based solar cells [28].

Usually, the organization of quantum rods described above has utilized controlled solvent evaporation as a means for surface aggregation. However, the surface organization of quantum rods driven by capillary forces or interplay of wetting–dewetting phenomena is very difficult to control and customize due to the complex balance of the weak interactions involved. Only a few examples of directed assembly of CdSe quantum rods into chains [29–31] or dimers and trimers [32] have been reported to date. However, such organized assembly required either a highly sophisticated procedure of cleavage of a single semiconductor nanolayer [29] or a complicated routine of weak complexation with DNA [31]. Moreover, the spatial areas of organized quantum rods still remained very limited (several microns square).

In this paper, we demonstrate control over CdTe quantum rod organization by changing the surface area available for their aggregation at the air–liquid interface followed by their transfer to a solid substrate by means of the Langmuir– Blodgett (LB) technique. This technique is a quite powerful assembly approach with several unique characteristics. First, a large area of ordered nanocrystal monolayer can be formed, which can be easily transferred to other substrates, and it is also fairly easy to carry out multiple or alternating layer deposition. In addition, the interparticle distance and the final superstructures can be finely tuned through control of the compression process, which could result in a wide range of properties such as the insulator-to-metal transition observed for a monolayer of silver nanocrystals [33, 34]. The LB method was previously exploited for the assembly of quantum dots [35, 36], BaCrO₄ [37] and gold [38] nanorods, and silver nanowires [39]. As opposed to the quantum dots, the LB assembly of quantum rods is especially interesting due to the anisotropic shape of the nanocrystals and their potential advantageous application in solar cells and other optoelectronic devices. Other nanorod materials previously used for LB experiments showed no or very weak optical properties with limited perspective use in optoelectronic applications. The use of the LB technique for the assembly of semiconductor nanorods has not been demonstrated.

Under increasing surface pressure, quantum rods form a domain morphology composed of round-shaped aggregates of monolayers of nanorods, which are subsequently transformed into elongated monolayered bundles and a continuous network. In contrast to previously reported attempts to form surface assemblies [20, 21, 24, 25], the LB technique allows forming ordered structures over large areas (centimeters across), transferring ordered CdTe monolayers onto various substrates, and encapsulating them in ultrathin polymer films which can be handled as free-standing structures. This last option is critical for the fabrication of large-scale optically active responsive arrays of encapsulated nanoparticles, as was demonstrated recently in our group [40–42].

2. Experimental details

2.1. Materials

Ultrapure water with a resistivity $\sigma > 18.0 \text{ M}\Omega$ cm (Barnstead Internationals) was used in the experiments. Silicon wafer substrates were cut to a typical size of 10 mm \times 20 mm and were cleaned in a piranha solution (1:3 (v/v) H_2SO_4/H_2O_2), according to the usual procedure adapted in our laboratory [43]. Attention: piranha solution is extremely dangerous and should be very treated carefully. Silicon wafers with {100} orientation and with one side polished (Semiconductor Processing Co.) and quartz plates with both sides polished (Chemglass Co.) were atomically smooth (microroughness within 1 μ m × 1 μ m surface area below 0.1 nm). After cleaning, the substrates were rinsed thoroughly with nanopure water and dried with dry nitrogen before they were used. The polyelectrolytes, poly(allylamine hydrochloride) (PAH), MW = 70000, and poly(sodium 4-styrenesulfonate) (PSS), MW = 70000, exploited for encapsulation of CdTe quantum rods were purchased from Aldrich and used without further purification.

2.2. Synthesis of CdTe quantum rods

CdTe quantum rods were prepared according to the known procedure [44]. Briefly, 200 mg CdO, 2.65 g trioctylphosphine oxide (TOPO), 0.82 g octyldecylphosphonic acid (ODPA) and 0.32 g octylphosphonic acid (OPA) were loaded into a three-neck flask. The mixture was degassed at $120 \,^{\circ}$ C under argon for 45 min. The reaction mixture was then heated to $320 \,^{\circ}$ C followed by the swift injection of 0.5 ml Te-TOP stock



Figure 1. UV–vis absorption spectra of a CdTe quantum rod cast layer (dashed line) and in chloroform solution (solid line).

solution. Te-TOP stock solution was prepared by dissolving 1.38 g Te powder in 12.5 g trioctylphosphine at elevated temperature. The reaction mixture was kept at 300 °C for 4 min and was allowed to cool down to 60 °C upon removal of heating mantle. Toluene (10 ml) was injected to form a concentrated stock solution. A minimum amount of isopropanol was added to precipitate the CdTe quantum rods. The precipitate was redispersed into chloroform. The concentration of the quantum rod solution was derived from the weight of dry residue after solvent evaporation. A cast quantum rod layer was obtained by drying a droplet of rod solution in chloroform on a transmission electron microscopy (TEM) grid.

2.3. LB monolayers

A KSV minitrough was used for the fabrication of LB monolayers and surface pressure–area $(\pi - A)$ isotherm collection. The compression rate was 5 mm min⁻¹ for all experiments. LB layers were deposited at various surface pressures onto a polished silicon wafer. For transmission electron microscopy (TEM) studies the LB monolayers were transferred on PAH-PSS multilayer film prepared by the layer-by-layer method on the top of a sacrificial cellulose acetate layer according to a well-established experimental procedure described elsewhere [45–47]. The TEM images were obtained after LB monolayers on layer-by-layer films were transferred onto a copper grid.

2.4. Characterization

Atomic force microscopy (AFM) images were collected using a Dimension 3000 AFM microscope (Digital Instruments) in the tapping mode according to the usual procedure adapted in our laboratory for ultrathin polymer films [48, 49]. AFM images were obtained with scan sizes ranging from 1 to 20 μ m. TEM was performed using a JEOL 1200EX electron microscope operated at 80 kV. Absorbance spectra of quantum rod solutions and ultrathin films were recorded using a Craig point-shot spectrophotometer attached to an optical fluorescent microscope (Leica DM4000M).



Figure 2. TEM image of a cast layer of CdTe quantum rods.



Figure 3. CdTe quantum rod length distribution derived from TEM image.

3. Results and discussion

3.1. Properties of CdTe quantum rods

The absorption spectrum of CdTe quantum rod solution in chloroform is shown in figure 1. The strong absorption maximum at 685 nm usually observed for CdTe quantum rods indicates their diameter being in the range 4–5 nm according to the literature data [26, 50]. The sharp and pronounced peak shows that the samples are relatively monodisperse in size and shape [51]. As is known, a decrease in lateral dimensions of CdTe quantum rods below 20 nm leads to a strong blue-shift in the absorbance spectrum due to the size confinement effect of the electron–hole transition [52].

The cast quantum rod monolayer obtained by drying the solution shows a similar absorption spectrum to that in solution (figure 1). Minor blue-shift can be caused by the coupling phenomenon related to the dense lateral packing of nanorods in the dry state. The absorption onset of CdTe in bulk at room temperature is in the range of 820–860 nm [53].

It should be noted that the quantum rod solution synthesized here showed light emission only during the earlier stages of the nanorod growth. The quantum rods grown did



Figure 4. Pressure–area isotherm of the Langmuir monolayer of CdTe quantum rods.

not possess pronounced photoemission either in solution or on solid substrates, which can be related to the minor changes of the CdTe crystal structure during the final stages of growth, not discussed here.

The TEM imaging of cast rods confirms the dimensions of CdTe quantum rods estimated from UV adsorption (figure 2). The average diameter was estimated to be 4.4 ± 0.5 nm, consistent with the estimation from UV-vis spectroscopy as

discussed above [26, 50]. The average length of quantum rods from TEM images is 24.6 ± 4.8 nm with modest ($\pm 20\%$) length distribution (figure 3). It is clear that there is some tendency to inter-rod organization after solvent evaporation with preferential end-to-end packing. This is probably caused by strong dipole–dipole interactions, which are known to be responsible for nanorod organization into regular structures or clusters [25].

3.2. Langmuir monolayers at the air-water interface

The surface pressure–area $(\pi - A)$ isotherm of the CdTe nanorod Langmuir monolayer demonstrates the surface behavior of quantum rods at the air–water interface upon increase of surface pressure (figure 4). The isotherm shows the transition point at a surface pressure of 25–30 mN m⁻¹, which can be an indication of the change in nanorod organization. The circles on the isotherm correspond to the specific surface pressures at which dipping experiments were made and LB monolayers were transferred to the silicon wafer. Representative examples of the microstructure at these pressures will be discussed below.

As is clear from these isotherms, the Langmuir monolayer of quantum rods can be compressed to a surface pressure as high as 65 mN m^{-1} before being collapsed (figure 4). On the other hand, the gradual increase in the surface pressure is observed for large surface area per nanorod. The limiting area



Figure 5. AFM ((a), (b)) and TEM (c) images of CdTe quantum rods at 3 mN m⁻¹. Image (b) and the left part of image (a) are height images (*z*-range 20 nm); the right part of image (a) is a phase image (*z*-range: 40°).

per molecule, A_0 , which indicates the onset of the formation of a dense monolayer is very high, reaching 5500 nm². This surface area exceeds the theoretical limiting area per quantum rod calculated from the nominal chemical composition of the material and the rod dimensions (200 nm²).

This discrepancy may be related to the presence of free surfactant molecules in the nanorod solution. In fact, although the original solutions of quantum rods have been precipitated after synthesis to remove the excess of ligands and redispersed again in chloroform, ligand molecules may still gradually dissociate from the CdTe surface over time after deposition on the water subphase, providing free ligand material which can fill the surface area between particles in the LB monolayer.

3.3. Microstructure of LB monolayers at different pressures

To elucidate the morphology and microstructure of LB monolayers, we conducted TEM and AFM imaging at different pressures, as indicated in figure 4. For further discussion we selected three representative surface pressures in gas, liquid, and condensed states. Here and later, CdTe quantum rod monolayers at different pressures were also transferred onto ultrathin polyelectrolyte films. The polyelectrolyte films containing an LB layer of nanorods were subsequently released from the surface by dissolving the sacrificial layer and transferred to TEM grids for TEM study.

As we observed, at very low surface pressure (3 mN m^{-1}) , at the onset of the increase of surface pressure, quantum rods within the LB monolayer form 'flower-like' aggregates with lateral size of 100–200 nm randomly distributed on the surface (figure 5). These aggregates represent a circle-shaped monolayer of quantum rods with the central portion composed of a few rods sitting on top of each other (figure 6). The circle-shaped aggregates represent a sort of flat 'micelle' on the substrate as evidenced in TEM images and high-resolution AFM images (figures 5(c) and 6). The aggregates are dispersed within the monolayer of excessive surfactant (mixture of TOPO, ODPA and OPA), which makes circle-shaped aggregates look like being locally associated on the large-scale AFM images (figure 5(a)).

At the intermediate surface pressures 20 and 32 mN m⁻¹, the surface density of circle-shaped aggregates increases significantly (figure 7). At 20 mN m⁻¹ the circle-shaped nanorod aggregates tend to lose their original shape and elongate. With further increase of surface pressure, the aggregates break up into smaller clusters with partially ordered quantum rods in the monolayer state. Although the overall morphology remains similar to that at lower pressure, some aggregates look like being composed of interconnected bundles of local uniformly oriented quantum rod clusters with densely packed rods (figure 7(d)). The breakage of round-shaped domains and formation of interconnected bundles corresponds to the transition point at the LB isotherm.

Further increase of the surface pressure (50 mN m^{-1}) leads to the denser packing of aggregates of various shapes. In the close proximity of an adjacent aggregate the edges of an aggregate become composed of multilayered nanorod bundles (figures 8(a) and (b)). The first indications of an



Figure 6. Cross-sectional analysis of a 1 μ m × 1 μ m image of CdTe quantum rods at a surface pressure of 3 mN m⁻¹. Arrows represent the thickness of the surfactant (mixture of TOPO, ODPA and OPA) layer (2.1 nm), the diameter of a single quantum rod (4.9 nm), and the thickness of an aggregate of three quantum rods on top of each other (14.1 nm).

interconnected network appear. The increase of surface pressure to 58 mN m⁻¹, which is close to the collapse pressure, further converts discrete aggregates into a well-defined, interconnected network (figures 8(c), (d)). A network is composed of bundles of locally oriented quantum rod aggregates with size on the order of 100 nm. This type of networking aggregation is observed for the highest surface pressure right before collapse, and thus presents the highest reachable surface density for a given chemical composition. Therefore, increasing the lateral compression causes dissociation of the initial domain morphology of flower-like aggregates and their rearrangement into interconnected continuous quantum rod bundles.

The formation of different types of nanorod aggregate within Langmuir monolayers is a result of the competition between rod-rod and quantum rod-water interactions



Figure 7. Topography AFM ((a), (b), (c)) and TEM (d) images of CdTe quantum rods at 20 mN m⁻¹ (a) and 32 mN m⁻¹ ((b), (c), (d)). The *z*-range for the AFM images is 20 nm.

under conditions of limited surface area available for their packing. It should be noted that rod-rod interactions dominate at any surface pressure, since at the very onset of increasing surface pressure the nanorods are already aggregated. However, at the same time, water-rod interactions make a significant contribution to the free energy of the system, especially at lower surface pressure. The indication for water-rod interaction is the assembly of nanorods into predominately monolayered aggregates as opposed to multilayered bundles (figures 5 and 6). Figure 5 may serve as the illustration for competing rod-rod and water-rod interactions. Most of the aggregate area corresponds to the nanorod monolayer, which is a result of water-rod interactions. However, in the center of almost every aggregate there is a bundle of nanorods sitting one on top of each other, which proves the domination of the rod-rod interactions. The increase of surface pressure leads to a decrease of the surface of water available for individual rods. As a result, the contribution of water-rod interactions decreases. In the ultimate case, at high surface pressure all nanorods are aggregated into multilayered bundles.

For a particle shelled with hydrophobic hydrocarbon chains (i.e., TOPO or OPA molecules), the initial distribution of chains around quantum rods is supposed to be uniform. However, placing the quantum rods at the water surface creates driving forces for the migration of loosely bound ligand molecules from the rod surface to avoid direct contact with water. This migration is possible due to the labile nature of the interaction of ligand molecules with the CdTe surface, as has been demonstrated [54]. Such reorganization within the hydrocarbon shell could result in the appearance of an excessive amount of ligand phase within the monolayer which is responsible for the dispersion of the initial round aggregates formed at low pressure. Apparently, some quantum rods remain trapped on top of the aggregates with shell-to-shell interactions favorable for multilayer packing in the centers of the individual aggregates at very low surface pressure.

Under compressive stresses, the initial isolated aggregates dissociate and merge into larger domains, composed of several circular interconnected aggregates, with a higher density of local packing. This morphology is further converted to a dense network-like morphology at even higher surface pressure. Further decrease of the surface area results in a denser packing of the aggregates and in the transformation of monolayered domains into 3D multilayered clusters, which form a continuous network of quantum rods.

Unlike previously reported promising data of nanorod assembly at an oil-water interface after evaporation of a solvent droplet [24], the results presented here possess several important features. As opposed to the LB technique, in the case of the drop cast method the nanorods are not uniformly compressed along the whole interface. Local compression forces here are caused by a high local concentration of



Figure 8. Topography AFM ((a), (b), (c)) and TEM (d) images of CdTe quantum rods at 50 mN m⁻¹ ((a), (b)) and 58 mN m⁻¹ ((c), (d)). The *z*-range of the AFM images is 50 nm.

nanorods in the conditions of evaporating solvent. As a result, the regions of ordered nanorod assembly are extremely small (on the order of microns). Besides, very different types of nanorod organization take place within one droplet. There is no doubt that the LB technique provides much wider opportunities for uniform, repeatable nanorod organization over much larger areas.

4. Conclusions

We have demonstrated the possibility of control over surface organization of semiconductor nanorods by means of the LB technique. The examples of nanorod organization include round-shaped and elongated domains composed of a monolayer of nanorods, as well as a continuous network of interconnected nanorod bundles. Such interconnected organization were preserved over large surface areas (several square centimeters) and the can be of interest for some applications in which the electronic and optical properties are critically dependent upon the percolation of semiconducting quantum rod bundles. Moreover, these 2D networks can be readily transferred to either semiconducting substrates or immobilized within freely suspended ultrathin polymer films for further handling and incorporation into microfabricated arrays.

Acknowledgments

This work was supported by the NSF-CBET-0506832 Grant, and the 3M Non-tenured Faculty Award (ZL). JX thanks the Institute for Physical Research and Technology of Iowa State University for a Catron graduate research fellowship.

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