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# Langmuir-Schaefer Deposition of Quantum Dot Multilayers

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The application of colloidal nanocrystals in various devices requires their assembly into well-defined mono- or multilayers. We explore the possibilities of the Langmuir–Schaefer technique to make such layers, using CdSe quantum dots as a model system. The layer quality is assessed using atomic force microscopy, transmission electron microscopy, and UV–vis absorption spectroscopy. For hydrophobic substrates, we find that the Langmuir–Schaefer technique is an excellent tool for controlled multilayer production. With hydrophilic substrates, dewetting induces a cellular superstructure. Combination with photolithography leads to micropatterned multilayers, and combination of different nanocrystal sizes allows for the formation of 2D binary superstructures.

# 1. Introduction

In the past 25 years, substantial progress has been made in the development of colloidal nanocrystal (NC) or quantum dot (QD) synthesis, leading to a controllable size, composition, shape, and surface chemistry.<sup>1–3</sup> Application of the unique QD properties in devices often requires the assembly of QDs. Single QD monolayers have been used in the design of light-emitting diodes (LEDs),<sup>4</sup> whereas QD multilayers are used for multicolored light-emitting films,<sup>5</sup> biosensors,<sup>6</sup> light-harvesting devices,<sup>7–9</sup> photodetectors,<sup>10</sup> Förster resonant energy transfer (FRET) sensing,<sup>11,12</sup> and LEDs.<sup>13</sup> A good control over the layer quality is essential for the efficiency of these devices,<sup>4,13</sup> and different approaches to achieve this have been reported.<sup>14</sup> For example, well-defined mono- or multilayers can be made using conventional

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layer-by-layer (LbL) assembly with<sup>15</sup> or without<sup>11</sup> polymer linker or by spin-assisted LbL assembly,<sup>16,17</sup> but all require watersoluble particles. For hydrophobic particles, an effective method to produce ordered QD monolayers is their self-assembly at the air-water interface, followed by either vertical deposition (Langmuir–Blodgett technique<sup>18</sup>) or horizontal deposition (Langmuir–Schaefer technique<sup>19</sup>) on a substrate. The Langmuir– Schaefer (LS) and Langmuir–Blodgett (LB) techniques provide important advantages over other solution-phase processing techniques such as drying-mediated assembly<sup>20</sup> and spin-coating,<sup>4</sup> as they allow deposition of closely packed QD layers of large areas, even on nonflat substrates.<sup>21</sup> Moreover, the resulting layers can be combined with LbL assembly,<sup>22</sup> used for subsequent microcontact printing,<sup>19,23</sup> or micropatterning through combination with photolithography.<sup>21</sup>

Despite the importance of the technique, little attention has been paid to the structure of QD LS multilayers. Using CdSe QDs (Q-CdSe) as a model system, we deposit mono- and multilayers on glass and silicon and assess the layer quality using atomic force microscopy (AFM), UV-vis absorption spectroscopy, and transmission electron microscopy (TEM). We find that the resulting layer structure is influenced by the substrate hydrophobicity: either smooth layers or cellular networks can be obtained. Smooth multilayers contain various stacking sequences and can be combined with optical lithography to create micropatterned multilayers. Finally, by combination of Q-CdSe with Fe<sub>3</sub>O<sub>4</sub><sup>24</sup> nanocrystals, we show how the LS technique enables the formation of 2D binary QD superlattices.

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## 2. Experimental Section

2.1. Nanocrystal Synthesis. Q-CdSe particles with a mean diameter of 3.1 and 3.4 nm were prepared based on the synthesis reported by Mulvaney and co-workers.<sup>25</sup> A selenium (Se, 99.999% Alfa Aesar) stock solution was made by heating a mixture of Se powder (0.1263 g, 1.6 mmol) in n-octadecene (ODE, 16 mL, 90% Alfa Aesar) under a nitrogen atmosphere at 195 °C for 2 h (until the mixture became orange-yellow). Then the mixture was cooled to room temperature, resulting in a transparent yellow solution which was stable for weeks. For the nanocrystal synthesis, cadmium oxide (CdO, 0.36 mmol, 99.999% Strem), oleic acid (OA, 3.6 mmol, 90% Sigma-Aldrich), and ODE (12 mL) were mixed and degassed for 1 h at 100 °C under nitrogen, followed by heating to 250 °C until all CdO dissolved. Then the solution was heated to 265 °C, and the Se stock solution (3.6 mL) was injected. The temperature of the mixture dropped after injection and the reaction continued at 235 °C for 4 min (diameter 3.1 nm, band gap absorption 544 nm) or 10 min (diameter 3.4 nm, band gap absorption 563 nm). After reaction, equal volumes of toluene and isopropanol were added, and the particles were precipitated by adding methanol. Afterward, the particles were further purified twice by resuspension in toluene and precipitation with methanol. Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles is reported elsewhere.<sup>2</sup>

**2.2.** Layer Deposition. Q-CdSe and Fe<sub>3</sub>O<sub>4</sub> monolayers were produced with a Nima 312D trough. Typically,  $30-50 \mu L$  of a QD suspension in toluene was spread dropwise on a water surface (250 cm<sup>2</sup>). Deinonized water with a resistivity above  $5 \times 10^4 \Omega$  m<sup>-1</sup> was used. The floating film was compressed at a rate of 10 cm<sup>2</sup> min<sup>-1</sup> until a pressure of 12 mN m<sup>-1</sup> was reached. The resulting layer was transferred to the substrate by gently stamping the substrate on the water surface containing the particles. As substrates we used glass microscopy slides and polished silicon cleaned with water and acetone. To obtain hydrophobic silicon, the native oxide of the silicon substrates was removed before deposition by etching with a 5% HF solution in water.

**2.3. Characterization.** The quality of the substrates and deposited layers was assessed with a variety of characterization methods at different stages during the process. AFM analysis was done with a Molecular Imaging PicoPlus system in ac AFM mode. TEM samples were prepared by holding a carbon-coated copper grid between a pair of tweezers and briefly letting the grid touch the nanocrystal film on the water surface. The samples were examined using a Jeol 2200 FS microscope. UV—vis spectra of nanocrystal suspensions and thin films were taken with a Perkin-Elmer Lambda 950 spectrophotometer.

**2.4. Micropatterning.** Local LS layer deposition was done by LS deposition on silicon substrates covered with patterned photoresist<sup>21</sup> with a thickness of 300 nm. Subsequent resist dissolution is done by dipping the sample in acetone (45 s), isopropanol (30 s), and distilled water (15 s).

### 3. Results and Discussion

**3.1.** Principle. Upon deposition of the Q-CdSe suspension on the water surface, the nanoparticles self-assemble into micro- and macroscopic monolayer islands with a surface of a few  $\mu m^2$  to several cm<sup>2</sup> (see Supporting Information S1). Compression of the film leads to merging of the monolayer islands into a continuous, closely packed monolayer. The typical surface pressure  $\pi$  vs surface area A isotherm obtained during compression allows monitoring of this process (Figure 1): early compression causes almost no increase in surface pressure (closing of the gaps and merging of monolayer islands), whereas further compression leads to a steep increase (close packed monolayer). At a surface



**Figure 1.**  $\pi$ -A isotherm of a Q-CdSe suspension spread on a water surface.



**Figure 2.** TEM images of Q-CdSe Langmuir–Schaefer mono-(a), bi- (b), and trilayers (c) deposited on a carbon-coated TEM grid at a surface pressure of  $12 \text{ mN m}^{-1}$ .



**Figure 3.** AFM image (a) and profile (b) of a Q-CdSe Langmuir– Schaefer layer deposited on silicon with native oxide. The FFT image produces a ring (c).

pressure of 19 mN m<sup>-1</sup>, the monolayer collapses. For this reason we choose to deposit the layers at a surface pressure of 12 mN m<sup>-1</sup>, which is within the close-packed monolayer regime but well below collapse pressure.

The transferred monolayers are homogeneous and free of microscopic voids over their entire area. AFM images show voidless, smooth films with few NC clusters (see Supporting Information S2). TEM images show close packed monolayers with local hexagonal order (Figure 2a). Some small holes (10-100 nm) may remain in the layer, resulting in an overall substrate coverage of 96–98% excluding point defects (see Supporting Information S3).

**3.2. Influence of Substrates.** Although the QD film on the air-water interface is a smooth monolayer, this is not always conserved after deposition. On hydrophilic substrates (glass, silicon with native oxide), we observed the formation of cellular networks (Figure 3a). These networks are similar to the structures observed due to drying-mediated self-assembly of nanocrystals,<sup>26,27</sup> except for the height: the structures reported in literature consist of QD monolayers, whereas the cross section in Figure 3b clearly shows higher structures. The origin of QD cellular

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networks has been attributed to spinodal decomposition,<sup>28,29</sup> nucleation and growth of holes,<sup>30</sup> or Marangoni convection.<sup>31,32</sup> A striking difference between these mechanisms and LS deposition is that with the latter dewetting occurs after evaporation of the spreading solvent (toluene) instead of during evaporation.

From a thermodynamics viewpoint, stamping a substrate on the floating monolayer implies the formation of substrate-QD and QD-water interfaces (see Supporting Information S5), each with their own surface energy. The free energy of these interfaces reads

$$\gamma_{\text{sub-OD}} A_{\text{sub-QD}} + \gamma_{\text{OD-water}} A_{\text{QD-water}}$$
(1)

with  $\gamma_{sub-QD}$  and  $A_{sub-QD}$  being the interfacial tension and surface area of the substrate-nanocrystal interface and  $\gamma_{OD-water}$  and  $A_{\rm QD-water}$  the surface tension and surface area of the nanocrystalwater interface. Dewetting introduces a substrate-water interface with area  $A_{sub-water}$  and surface tension  $\gamma_{sub-water}$ . Then, the energy corresponding to the creation of the different interfaces becomes

$$\gamma_{\text{sub-QD}}A_{\text{sub-QD}} + \gamma_{\text{QD-water}}A_{\text{QD-water}} + \gamma_{\text{sub-water}}A_{\text{sub-water}}$$
 (2)

If  $\gamma_{sub-QD}$  is larger than  $\gamma_{sub-water}$ , as expected for hydrophobic particles on a hydrophilic substrate, dewetting (i.e., reduction of  $A_{\text{sub-OD}}$  and increase of  $A_{\text{sub-water}}$  is favorable. Despite the occurrence of dewetting, the QD-substrate interaction is surprisingly strong. In the case of silicon with native oxide, immersion of the substrates with cellular networks on top in toluene for 45 s results in the resuspension of all nanocrystals, except the ones in direct contact with the substrate. This results in monolayer-thick cellular networks, as shown in the Supporting Information (S8).

The faint ring in the Fourier transform image (Figure 3c) of the network in Figure 3a shows that dewetting occurs on a characteristic length scale and results in a preferred intercellular separation.<sup>27</sup> Therefore, these networks have been suggested as a nonlithographic nanopatterning technique.<sup>30</sup> In this respect, LS deposition offers the possibility of producing multilayer networks.

**3.3.** Multilaver Deposition. LS multilaver deposition was achieved by repetitive stamping of substrates on different areas of the floating layer. For optical characterization, mono- and multilayers were deposited on glass substrates, with a 50 nm poly-(methyl methacrylate) spin-coated layer to avoid dewetting. Photoluminescence experiments show no emission from the layers, probably due to oxidation of the particles during the deposition experiment. Figure 4a shows UV-vis absorption spectra of the deposited layers. The absorption spectra of the thin films are similar, though slightly red-shifted, as compared to the spectra of the particles in suspension (see Supporting Information S4). Figure 4b shows a linear trend between the absorbance and the number of deposited layers. This indicates uniform deposition, unlike results reported from layer-by-layer deposition<sup>6,33</sup> or Langmuir–Blodgett deposition, where the upward and downward stroke may result in a different transfer ratio.<sup>34</sup> A single floating monolayer can be used to coat multiple samples or to coat a single substrate with a multilayer, enabling an efficient nanoparticle use. Interestingly, UV-vis spectra of hydrophilic

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Figure 4. UV-vis absorption spectra of PMMA-coated glass slides containing Q-CdSe Langmuir-Schaefer mono- and multilayers (a). The absorption scales linearly with the number of deposited layers (b).



Figure 5. TEM image of a Q-CdSe LS bilayer showing different stacking mechanisms. The most observed are AB stacking (b) and linear stacking (c). Both stacking mechanisms are accompanied by a schematic representation (d and e).

glass containing cellular networks yield similar results. This means that the higher roughness created by dewetting does not affect the transfer efficiency for the next depositions. Adding extra layers mainly leads to a conformal coating of the existing structures, more than the creation of new cells (see Supporting Information S7 and S8).

The high degree of similarity between the absorption spectra of the LS layers and the colloids in chloroform means we can compare the extinction coefficient of the particles in these two cases. We calculate the extinction coefficient of the colloidal particles, using the solvent refractive index and optical constants of bulk cubic CdSe at short wavelength (340 nm), and the Maxwell-Garnett effective medium theory.<sup>35</sup> The resulting values are consistent with values obtained by combining TEM, UV-vis absorption spectroscopy, and inductively coupled plasma mass spectroscopy.<sup>36</sup> Using the same extinction coefficient values for the thin films leads to concentrations two or three times higher than expected for a hexagonally ordered layer (see Supporting Information). This implies that QDs in the monolayer absorb 2-3 times stronger than QDs dispersed in chloroform. Returning to the Maxwell-Garnett effective medium theory and using the formula of Ricard et al.,<sup>37</sup> this implies that particles in a close-packed film experience less screening of the electrical field (higher local field factor) than particles in suspension.

TEM images of Q-CdSe LS mono-, bi-, and trilayers show a homogeneous coating (Figure 2). As with the monolayers, the multilayers are closely packed and only show short-range order. Interestingly, the deposition of a second layer of particles is not

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**Figure 6.** AFM image (a) and profile (b) of a patterned Q-CdSe bilayer.

random with respect to the first layer, and different stacking sequences can be identified. The structure in Figure 5b results when the second nanocrystal layer with hcp ordering is rotated by 30° with respect to the underlying one. The arrangement in Figure 5c is obtained when the second layer is shifted by half of the lattice constant in vertical direction with respect to the underlying layer. Multilayer deposition leads to the combination of various stacking sequences and thus to a complex layer architecture. The various stacking sequences, however, do not affect the structural integrity of the film: once deposited the particles do not rearrange and the layers do not crack or peel off of the substrate.

3.4. Micropatterning. Earlier work showed that LB deposition enables the coating of nonflat substrates. This was used for example to obtain micropatterned monolayers through combination with photolithography.<sup>21</sup> Also with deposition of LS Q-CdSe mono- and multilayers, we observed conformal coating of nonflat substrates. Again the photolithography approach was used to obtain local deposition: LS mono- and multilayers were deposited on silicon substrates containing developed photoresist. This was followed by resist dissolution, thus removing all nanocrystals but those directly deposited on the bare silicon. Figure 6a clearly shows that structures with dimensions of 5  $\mu$ m can be deposited in this way, and from line profiles it can be concluded that the deposited layer is a bilayer (Figure 6b). For resist dissolution acetone, isopropanol and water were used. The process does not lead to the formation of cracks or holes in the film, indicating strong LS film adherence and robust layers.

3.5. Binary Layers. Applications like FRET-based lightharvesting devices require multilayers containing different types of nanocrystals.<sup>8</sup> LS deposition is not limited to multilayers of one type of nanocrystals and is thus an option for realizing such applications. Moreover, control of the interparticle distance in each layer (by changing the particle diameter and/or ligand length) may enable formation of ordered binary structures. To demonstrate this, we deposited a monolayer of oleic acid-capped Fe<sub>3</sub>O<sub>4</sub> nanoparticles (interparticle distance 9.3 nm) on a TEM grid, followed by the deposition of a Q-CdSe monolayer (interparticle distance 4.8 nm). TEM images show not only that it is possible to combine the two types of monolayers but also that the potential energy surface created by the bigger underlying nanoparticles influences the positions of the nanoparticles in the upper layer (Figure 7a). With an interparticle distance ratio of  $\sqrt{3}$ the formation of a 2D crystal where the particles of the upper layer occupy the A, B, and C positions of the lower layer should be possible (Figure 7b,c). In this way, the small dots fill the gaps in the monolayer of the large lower dots, with one excess small dot on top of every large one. Although in our example the distance ratio is 10% larger than  $\sqrt{3}$ , many of the Fe<sub>3</sub>O<sub>4</sub> nanocrystals are indeed surrounded by six CdSe particles, occupying B and C



Figure 7. TEM image (a), detail (b), and corresponding schematic representation (c) of a Fe<sub>3</sub>O<sub>4</sub>/CdSe Langmuir–Schaefer binary layer, with an interdot distance ratio around  $\sqrt{3}$ . The smaller Q-CdSe particles of the upper layer occupy the A, B, and C positions of the lower layer of larger Fe<sub>3</sub>O<sub>4</sub>.



**Figure 8.** TEM image (a) and details (b, c)  $Fe_3O_4/CdSe$  Langmuir–Schaefer binary layer. Defects in the binary layer are mainly induced through defects in the first layer, such as grain boundaries (b) and point defects (c).

positions and have one CdSe particle on top. This suggests that on top of making multilayers LS deposition may also lead to binary 2D QD superlattices. The 3D counterparts of such superlattices are usually produced by controlled evaporation of colloidal QD suspensions.<sup>38–40</sup> Although LS deposition is probably limited to superstructures with 2D symmetry, it has many advantages: it offers easy control of particle stoichiometry, combination of nanoparticles suspended in incompatible solvents, coating of large areas, and less control over atmospheric conditions is required during deposition. The ratio of the interdot distances, however, is still important, as large deviations from the ideal value result in unordered structures.

In areas where the underlying layer of larger particles is well ordered, few defects in the binary layer are observed. On the other hand, defects in this first layer induce defects in the final binary layer. This means that besides the interdot distance ratio, also the quality of the first layer is essential to the amount of stacking faults in the binary layer. The first layer therefore really acts as a template layer. As an example, Figure 8 shows TEM images of a

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binary lattice where three hexagonally ordered grains in the lower (template) layer meet in the center of the image. Clearly, the resulting disorder in the template layer is transferred to the top layer (Figure 8b). Also in Figure 8, a point defect in the template layer is visible (Figure 8c), again leading to a loss of ordering between the template and the top layer.

### 4. Conclusions

We made NC mono- and multilayers using LS deposition, with Q-CdSe particles as a model system. AFM and TEM images show that the obtained layers are smooth and closely packed. On hydrophilic substrates monolayer dewetting is observed. Although the obtained cellular networks may be useful for non-lithographic micropatterning, deposition of monolayers on such substrates works better with Langmuir–Blodgett deposition. LS multilayers are made by simple multiple stamping of a substrate on the floating Langmuir layer. The resulting layers are uniform, as shown by UV–vis absorption experiments. Deposition of a second layer does not occur at random, but different stacking mechanisms are possible, resulting in complex multilayer architectures. Changing the relative sizes of the nanocrystals improves stacking homogeneity, and 2D binary superstructures can be obtained by careful control of the interdot distance ratio. Finally,

combination of LS deposition and optical lithography allows multilayer micropatterning. This makes LS deposition an easy, efficient, and versatile technique to obtain NC multilayers, which may be particularly useful in the design of light-harvesting devices.

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**Supporting Information Available:** AFM and lowmagnification TEM images of Q-CdSe monolayers, further characterization of dewetted layers, and calculation of particle density and concentration. This material is available free of charge via the Internet at http://pubs. acs.org.