

# Lateral Patterning of CdTe Nanocrystal Films by the Electric Field Directed Layer-by-Layer Assembly Method

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Received September 28, 2001. In Final Form: January 8, 2002

The electric field directed layer-by-layer assembly (EFDLA) method is used to fabricate a pattern of two different types of CdTe nanocrystals on a structured indium–tin–oxide (ITO) substrate. Such a pattern can be used to fabricate pixel arrays of CdTe light-emitting devices that emit electroluminescence of different colors. The highly fluorescent CdTe nanocrystals are negatively charged and alternated by a polycation, poly(diallyldimethylammonium chloride) (PDDA), in the fabrication of multilayer PDDA/CdTe films on ITO and Au surfaces by the EFDLA method. The depositions of the charged species on different electrodes are controlled by the polarity of an applied bias voltage. We define the deposition that becomes easier in the electric fields as favorable deposition and that becomes more difficult as unfavorable deposition. Experimental results obtained by quartz crystal microbalance reveal that a series of unfavorable depositions of CdTe and PDDA performed in an alternate way can at most result in one bilayer of PDDA/CdTe on the Au surface at 0.6 V, whereas favorable depositions show a net growth of deposited mass with the increased number of deposition cycles. Similar results can also be obtained by using ITO electrodes, but a relatively high voltage of 1.4 V is required to achieve a contrast of 99% between favorable and unfavorable depositions. The large contrast enables the fabrication of dual-color photoluminescence and electroluminescence patterns of PDDA/CdTe films by successively depositing two differently sized CdTe nanocrystals on different ITO electrodes on one common substrate by the EFDLA method.

## Introduction

Over the past decade, great efforts have been undertaken to produce well-defined ultrathin molecular films for exploring their potential in optoelectronic devices and chemical and biological sensors.<sup>1–4</sup> Layer-by-layer (LbL) self-assembly has been demonstrated to be a promising method in many applications due to its low cost and simplicity in ultrathin film preparation, its capacity in producing large area films, and its ability in achieving good reproducibility for the film quality and physical properties.<sup>5</sup> In addition, the LbL self-assembly method is unique for combining different types of materials such as polyelectrolytes, anionic and cationic bipolar species, inorganic nanoparticles, dyes, proteins, DNA, and conducting polymers into one ultrathin film system.<sup>6–13</sup> Thus,

it represents one of the key techniques in the so-called bottom-up strategy pursued in modern nanotechnology. Moreover, the LbL self-assembled films typically exhibit a much better film quality than the thin films prepared by the Langmuir–Blodgett technique or spin coating and casting methods. All these advantages make the LbL self-assembled systems particularly promising in optoelectronic applications.

A high degree of control has been achieved for LbL self-assembly along the normal direction of the film.<sup>14,15</sup> In contrast, the possibilities to control the formation of lateral structures or patterns are still limited. P. Hammond and co-workers have been very successful in fabricating a lateral patterning structure for LbL self-assembled films.<sup>16,17</sup> Their strategy is to use a soft lithography technique to form patterned surfaces of self-assembled monolayers (SAMs) on which the LbL self-assembled film is subsequently constructed. Although satisfying results have been achieved, this soft lithography approach is still limited in making binary and tertiary patterns of different types of self-assembled films. By forming hydrophilic–hydrophobic patterns of self-assembled monolayers using the soft lithography method, thin layers of hydrophilic and hydrophobic CdSe nanocrystals of different sizes can be selectively deposited on different sites to form a binary pattern.<sup>18</sup> However, to further improve the quantities loaded in different sites is challenging. But one molecular

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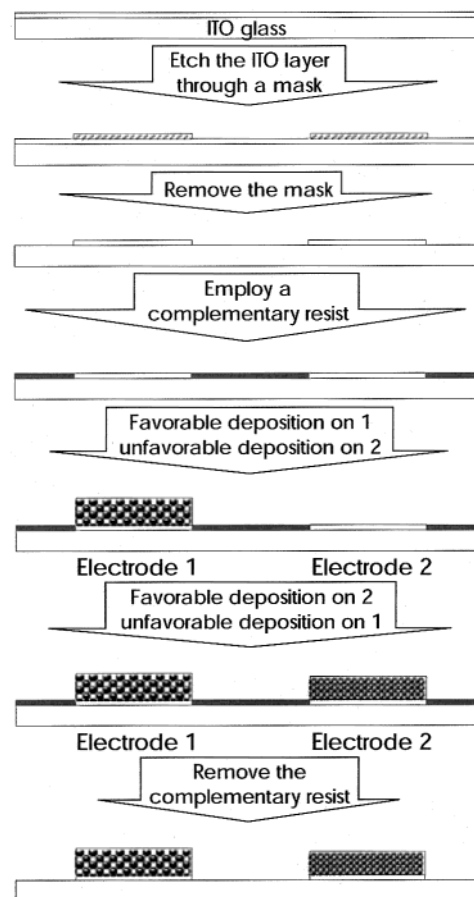
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layer of nanoparticles is not sufficient for many applications. Another successful approach for fabricating binary and even tertiary patterns of different types of nanocrystals is reported by J. Heath and co-workers using a combinatorial approach.<sup>19,20</sup> The main procedures of their method are to first cover a solid surface with an organic monolayer containing photolabile protection groups and then by a lithographic masking technique to develop patterns of spatially and chemically distinct interaction sites for different types of nanocrystals. Since the developing and assembling procedures can be performed step by step, multiple patterns can be realized. But to our best knowledge, this method has not yet been adopted for fabricating patterns of ionically LbL self-assembled films.

Very recently, we have developed an EFDLA (electric field directed layer-by-layer assembly) method for fabricating patterns of LbL self-assembled films on conducting substrates.<sup>21,22</sup> The basic idea is to use an electric field to direct the spatially selective deposition of LbL self-assembled films. Highly fluorescent CdTe nanocrystals of different sizes and a polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), are used to demonstrate the feasibility of this novel method. Binary patterned arrays of LbL self-assembled films consisting of two differently sized CdTe nanocrystals are obtained by a two-step deposition using the EFDLA method on indium–tin–oxide (ITO) electrodes. Here, potential applications of such binary arrays of differently sized CdTe nanocrystals are demonstrated by fabricating various types of light-emitting pixels that emit light of different colors on a common substrate.

### Experimental Section

The key issue of using the EFDLA method to realize spatially selective deposition is how to control the start and stop of the ionically LbL self-assembling process on different areas of a substrate in order to eventually prepare spatially separated lateral patterns. It is well-known that electric fields can accelerate and decelerate the deposition of charged species on an electrode.<sup>23–26</sup> This is the basis of the electrophoretic deposition technique. If the accelerating and decelerating effects are large enough, control over the start and stop of the film growth driven by electrostatic attraction can be realized on electrodes.<sup>21,22</sup> Moreover, if a series of electrodes are placed on the same substrate and spatially separated, one can deposit different types of films on different electrodes by programming the polarities on each single electrode. Using successive depositions of different materials, spatially separated patterns can eventually be formed. This is the basic idea for achieving independent patterns of different types of self-assembled films on a common substrate by the EFDLA method. For the convenience of illustration, we denote the electrode on which film deposition is accelerated by electric fields as the working electrode, whereas the electrode on which the deposition is decelerated is denoted as the counter electrode. Therefore, favorable deposition always takes place on the working electrode and unfavorable deposition occurs on the counter electrode. In



**Figure 1.** Preparative procedures for successive depositions of two differently sized CdTe nanocrystals on two different electrodes by the EFDLA method.

practice, the favorable deposition is realized by setting the polarity on the working electrode opposite to the sign of the charges on the deposited material. The unfavorable deposition is realized just by the opposite way. Thus, selective deposition of CdTe/PDDA alternate multilayer films on the working electrode rather than on the counter electrode can be realized by enabling a series of favorable depositions on the working electrode. This requires switching of the polarity of the working electrode between positive and negative polarities each time the working electrode is transferred from the solution of negatively charged CdTe particles to the solution of positively charged PDDA. The main preparative procedures for binary patterned arrays are outlined in Figure 1. ITO glass with a sheet resistance of  $30 \Omega/\square$  was used as the electrode and the film substrate as well. Two 2-mm ITO stripes separated by a 2-mm nonconducting stripe were obtained by chemically etching the ITO glass through a mask. The lateral structures of the ITO substrate are shown in Figure 2. Typically, the glass area was protected by a removable resist during the film deposition in order to get rid of photoluminescence (PL) color interference from deposition occurring between the electrodes.

Negatively charged highly fluorescent CdTe nanocrystals and positively charged PDDA were used to prepare multilayer PDDA/CdTe films [(PDDA/CdTe)<sup>*n*</sup>] in the presence of electric fields. Typical concentrations of the CdTe and PDDA solutions were  $1.3 \times 10^{-3}$  M (with respect to Cd<sup>2+</sup>) and  $5 \times 10^{-2}$  M (with respect to the repeat unit of PDDA), respectively. The pH value of the CdTe particle solution was  $7.8 \pm 0.2$ . The CdTe stabilized by thioglycolic acid was synthesized according to ref 27. Since the acid group from the thioglycolic acid is pointing to the aqueous environment while the thiol group binds to the CdTe particle surface, in a very large pH range the resultant CdTe nanocrystals

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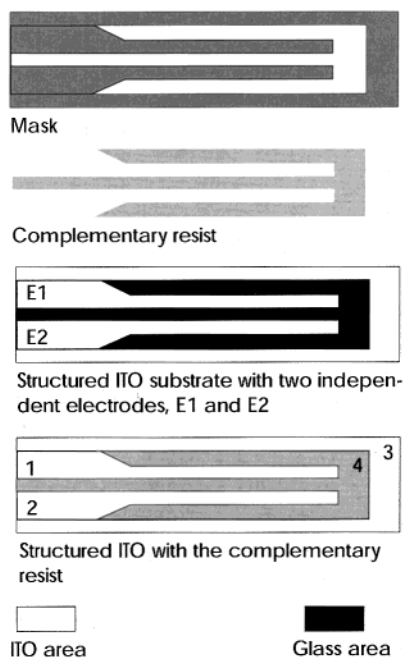
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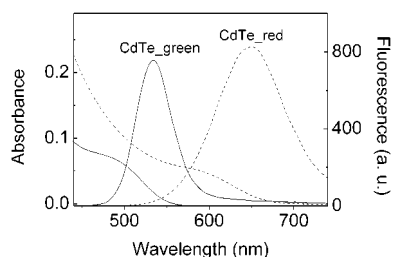
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**Figure 2.** Lateral structures of the structured ITO substrate that is used in the fabrication of the dual-PL-color pattern of CdTe nanocrystals.

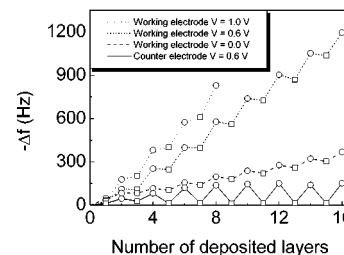


**Figure 3.** Absorption and fluorescence spectra of two differently sized CdTe nanocrystals which are named as CdTe\_green and CdTe\_red according to their PL colors.

are negatively charged. The thioglycolic acid stabilized CdTe nanocrystals exhibit a particle size dependent PL color due to the quantum confinement effect.<sup>27–29</sup> By tuning the particle size from 2.5 to 3.5 nm, the PL color can be effectively tuned from green to red. The absorption and fluorescence spectra of green- and red-emitting CdTe particles (CdTe\_green, CdTe\_red) are shown in Figure 3. Since the PL emissions from the CdTe\_green and CdTe\_red are clearly distinguishable, they were used to check the effectiveness of the pattern formation.

In general, the EFDLA deposition was performed by the same procedures as the traditional LbL self-assembling process except that a dc voltage was applied during the film deposition. A two-electrode system was adopted with electrodes being either in a face-to-face or in a side-by-side arrangement. No difference was practically observed between these two types of electrode arrangements with respect to the effectiveness of the EFDLA deposition.<sup>21,22</sup> In detail, the working electrode was connected to the negative pole of the dc power supply during the deposition of PDDA. After 5 min of deposition, the electrode assembly was immersed in Milli-Q water for 3 min in order to remove the excessive adsorption. Then another 5 min of deposition in the CdTe solution was performed while the polarity of the working electrode was switched to positive. The deposition of CdTe was then followed by the same cleaning procedure as mentioned above. By repeating the depositions of PDDA and CdTe in the presence of electric fields in an alternate fashion, a multilayer film can be deposited on the working electrode.

Quartz crystal microbalance (QCM) and fluorescence spectroscopy were used to characterize the effectiveness of spatially



**Figure 4.** Frequency decrease ( $-\Delta f$ ) induced by the adsorption of (PDDA/CdTe)\* $n$  films on the QCM electrodes recorded at different working voltages, i.e., 0, 0.6, and 1.0 V.

selective depositions of PDDA/CdTe multilayer films on Au and ITO electrodes, respectively, in electric fields. A homemade QCM was used to monitor the mass changes on both the working electrode and the counter electrode during the deposition of CdTe and PDDA by the EFDLA method. Quartz crystal resonators (9 MHz) were employed. Glass caps were used to cover one of the Au electrodes on the resonator in order to get rid of the interference from the deposition that is not controlled by the electric fields. Two such resonators were then fixed at a 4 mm distance with their unsealed electrodes facing each other during the EFDLA deposition.

Electrochemical stability is a mandatory prerequisite when electric fields are applied to control the CdTe film deposition. Cyclic voltammetry was used to investigate the electrochemical stability of the CdTe nanocrystals. In electrochemical experiments, the concentration of CdTe was  $6.5 \times 10^{-4}$  M (with respect to the Cd<sup>2+</sup>). Na<sub>2</sub>SO<sub>4</sub> serving as supporting electrolyte was added into the CdTe solution at a concentration of 0.05 M. The electrochemical experiments were performed in a one-compartment three-electrode cell with a standard Ag/AgCl (3 M KCl) electrode (211.5 mV vs standard hydrogen electrode, 20 °C) as a reference. A platinum wire and carefully cleaned ITO glass served as the counter electrode and the working electrode, respectively.

By successively depositing (PDDA/CdTe\_red)\* $n$  and (PDDA/CdTe\_green)\* $n$  films on the two ITO electrodes shown in Figure 2, arrays of dual PL colors were fabricated.

Fluorescence and UV–visible spectra of CdTe nanocrystals and PDDA/CdTe films were measured using a Varian Cary 50 spectrometer and a Varian Cary Eclipse, respectively. The morphology of the resultant film surface was characterized by atomic force microscopy (AFM) using tapping mode. The film thickness was measured by cross-sectional scanning electron microscopy (SEM) (JEOL JSM-6400). A conventional potentiostat, Autolab PGStat 12 from Eco-Chemie in The Netherlands, was used in the electrochemical experiments.

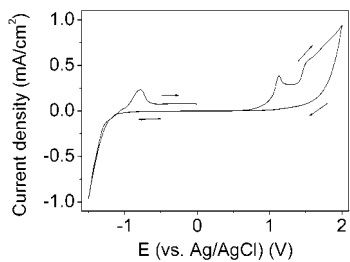
## Results and Discussions

The QCM results on selective depositions on Au electrodes controlled by electric fields are given in Figure 4. The diagram shows the frequency changes recorded from two resonators that acted as working and counter electrodes during the deposition of (CdTe/PDDA)\* $n$  films. After deposition of the first five layers at a voltage of 0.6 V, that is, three layers of PDDA and two layers of CdTe, the following unfavorable deposition of CdTe leads to a constant decrease in frequency. The subsequent unfavorable deposition of PDDA however raises the frequency to its initial value again. This indicates that at most one bilayer of PDDA/CdTe can be deposited on the counter electrode under unfavorable deposition. In contrast, the depositions of CdTe and PDDA by favorable deposition result in a linear frequency decrease. This suggests that the loaded mass increases linearly with the increased number of dipping cycles. Therefore, it can be concluded that electric fields can effectively control the ionically self-assembling processes of PDDA and CdTe and finally give rise to a huge mass contrast between films obtained by the favorable and unfavorable depositions, respectively.

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**Figure 5.** CVA curve recorded from an aqueous solution of CdTe<sub>red</sub> nanocrystals at a potential scanning rate of 10 mV/s.

**Table 1. Fluorescence Contrast  $C$  between 10-Bilayer PDDA/CdTe Films [(PDDA/CdTe)\*10] Formed by Favorable and Unfavorable Depositions and the Surface Roughness of (PDDA/CdTe)\*10 Films Obtained by Favorable Depositions**

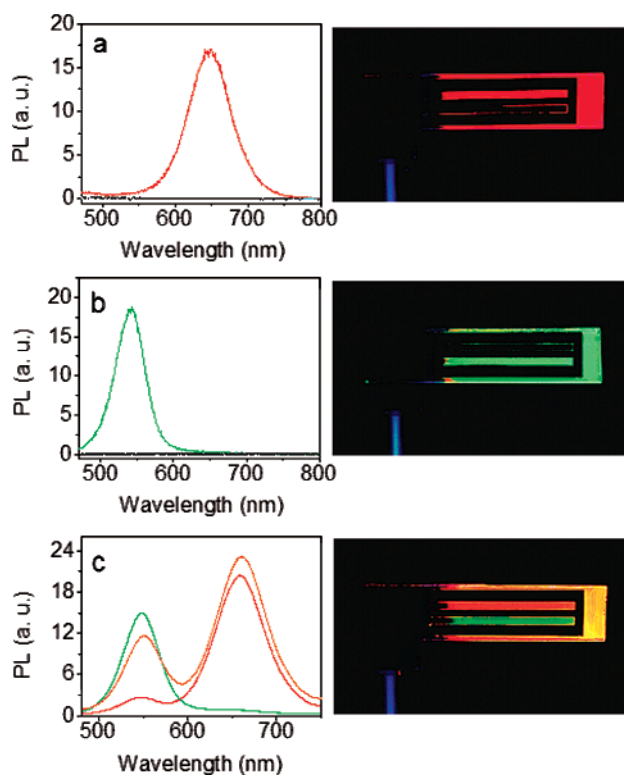
|                        | applied voltage (V) |     |      |      |      |      |      |      |
|------------------------|---------------------|-----|------|------|------|------|------|------|
|                        | 0.6                 | 0.8 | 1.0  | 1.2  | 1.4  | 1.6  | 1.8  | 2.0  |
| contrast (%)           | 5.7                 | 8.3 | 28.1 | 48.1 | 98.8 | 98.7 | 98.8 | 96.8 |
| surface roughness (nm) | 9.5                 | 9.1 | 10.8 | 12.8 | 13.9 | 14.3 | 38.7 | 35.8 |

In addition, the loaded mass on the working electrode also increases with the increase of the external voltage as shown in Figure 4. More detailed investigations reveal that the increase of the loaded mass achieved at higher voltage is a result of mass increases affecting both the CdTe and the PDDA films.<sup>22</sup>

The selective deposition of PDDA/CdTe films on ITO electrodes by the EFDLA method exhibits a different voltage dependence from that observed on Au electrodes. In general, higher bias voltages are required in order to get 99% contrast between favorable and unfavorable deposition. Since CdTe nanocrystals can be electrochemically degraded at high voltage, the electrochemical stability of CdTe becomes critical for realizing the EFDLA deposition on ITO electrodes. A typical CVA curve recorded from the red-emitting CdTe solution is given in Figure 5. There is an approximately 1.5 V potential window between  $-0.8$  and  $+0.7$  V (vs Ag/AgCl (3 M) electrode) where nearly no evident electrochemical reaction takes place. It was observed that voltages above 2.0 V led to degradation of the ITO electrode and failure of the deposition.

The effectiveness of selective deposition of PDDA/CdTe multilayer films on ITO electrodes guided by the electric fields was characterized by fluorescence spectroscopy. A quantitative description of the selectivity is given by a fluorescence contrast  $C = (I_f - I_u)/(I_f + I_u)$ , where  $I_f$  and  $I_u$  are the fluorescence peak intensities of (PDDA/CdTe)- $n$  films obtained under favorable and unfavorable depositions, respectively. Experimental values for the fluorescence contrast as a function of applied voltage are summarized in Table 1. The fluorescence contrast  $C$  increases with the increase of voltage and reaches nearly 99% when the voltage is raised to 1.4 V, and then it undergoes a slight decrease upon further increase of voltage. This indicates a faster degradation of CdTe nanocrystals on the working electrode at voltages higher than 1.4 V.

The destructions of the ITO electrode as well as the PDDA/CdTe film on the working electrode are also reflected by the voltage-dependent surface roughness of the resultant films deposited on the working electrode. The experimental data on surface roughness given in parallel to the fluorescence contrast  $C$  in Table 1 were derived from AFM measurements. The surface roughness is defined as the square root of the standard deviation of



**Figure 6.** Photographs of the lateral structures formed by CdTe<sub>green</sub> and CdTe<sub>red</sub>: (a) (PDDA/CdTe<sub>red</sub>)\*40 (sample A), (b) (PDDA/CdTe<sub>green</sub>)\*40 (sample B), and (c) (PDDA/CdTe<sub>red</sub>)\*40|| (PDDA/CdTe<sub>green</sub>)\*60 (sample C). The fluorescence spectra recorded from the electrodes as well as the marginal area in the case of sample C are given in the frames parallel to the PL images.

film height at the film surface. In general, it increases with the increase of voltage. However, when the voltage exceeds 1.6 V, the roughness increases dramatically. The general increase in surface roughness is mainly caused by a faster deposition under higher voltage conditions. As a result, with the increase of voltage the CdTe nanocrystals can find less and less time to arrange themselves to a proper position to flatten the film surface. A similar behavior was observed in the electrophoretic deposition of SiO<sub>2</sub> particles.<sup>30</sup> The sharp increase in roughness at around 1.6 V may be the result of deconstruction of the CdTe films due to electrochemical degradation of CdTe nanocrystals.

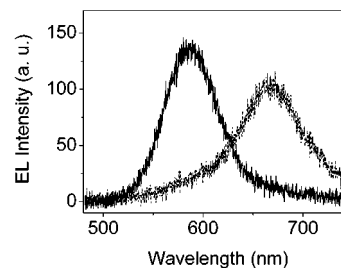
On the basis of all of the above-mentioned results, the working voltage of 1.4 V was adopted for the preparation of single-PL-color and dual-PL-color patterns of PDDA/CdTe films by the EFDLA method. Fluorescence images of 40-bilayer PDDA/CdTe<sub>green</sub> (sample A) and 40-bilayer PDDA/CdTe<sub>red</sub> (sample B) films selectively deposited on one electrode on the structured ITO substrate shown in Figure 2 are presented in Figure 6. Figure 6c was recorded from a dual-PL-color sample (sample C) obtained by successively depositing 40-bilayer CdTe<sub>red</sub>/PDDA and 60-bilayer CdTe<sub>green</sub>/PDDA on two different electrodes on one substrate. In parallel to the PL images, PL spectra recorded from different electrodes are presented. In Figure 6c, a PL spectrum recorded from the orange margin of the substrate is additionally presented. The marginal areas (area 3 indicated in Figure 2) are the locations where no

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electric fields were present to control the film growth. Therefore, the deposition of both CdTe<sub>red</sub> and CdTe<sub>green</sub> was allowed there and resulted in a PL color of orange. The dark areas (area 4 indicated in Figure 2) between the electrode and the marginal areas are protected by the removable resist during the film deposition. Due to the misalignment of the complementary resist on the ITO structures, a thin gap became available for the freely self-assembled films and thus gave rise to a thin color line around the counter electrode on samples A and B. In practice, the misalignment can be avoided, but here it makes the counter electrode visible since there is nearly no PL observable from the counter electrode on samples A and B. Cross-sectional SEM results confirm that the difference between the films obtained by favorable deposition and unfavorable deposition is mainly determined by the film thickness.<sup>21</sup> SEM results show that a 40-bilayer PDDA/CdTe<sub>red</sub> film deposited on an ITO working electrode under 1.4 V has a thickness of about 140 nm. In contrast, nearly no film is deposited on the counter electrode. The film thickness obtained under the same dipping conditions using the traditional LbL self-assembly method (without any applied voltages) is about 100 nm.

A careful examination of the fluorescence spectra recorded from the red and green electrodes in Figure 6c shows that the fluorescence contrast is not as perfect as that shown in Figure 6a,b, where the sample was dipped only in *one* solution of CdTe with a fixed mean particle size. This implies that the unfavorable deposition is slightly less controllable on top of the CdTe film than on a bare electrode. Nevertheless, the large PL contrast between the two electrodes offers great potential to the EFDLA method for achieving binary and even tertiary independent patterns of different types of self-assembled films on one substrate.

One potential application of the lateral patterns of differently sized CdTe nanocrystals is their use in electroluminescent nanocrystal pixels that emit different colors of light. It has been shown by various groups that highly fluorescent II–VI nanocrystals can be used as emitting materials in light-emitting devices.<sup>31–34</sup> Successful preparations of pixels consisting of different types of semiconductor nanocrystals open a very elegant definition of different colored pixels in display applications. No lithographic steps are needed after the initial definition of the ITO electrodes. Electroluminescence (EL) pixels of PDDA/CdTe<sub>red</sub> film and PDDA/CdTe<sub>green</sub> film were then prepared by evaporating aluminum through a 2 mm wide gap which was aligned perpendicularly to the ITO stripes to sandwich the PDDA/CdTe films in between. The thickness of the Al electrode was  $140 \pm 20$  nm. The EL measurements were performed with the aid of a fluorescence microscope coupled to a CCD camera. Figure 7 shows two electroluminescence spectra recorded from



**Figure 7.** Electroluminescence spectra recorded from two adjacent pixels that are formed by (PDDA/CdTe<sub>green</sub>)\*60 and (PDDA/CdTe<sub>red</sub>)\*40 films. The EL spectra are recorded under a forward bias of 5 V.

two adjacent pixels of PDDA/CdTe<sub>red</sub> and PDDA/CdTe<sub>green</sub> films. The EL spectra from these two pixels are clearly distinguishable and show an even higher emission contrast than the corresponding PL emissions. In addition, a small red-shift of the EL spectrum with respect to the PL spectrum is observed. Such shifts have been reported before.<sup>32</sup> It is mainly caused by oxidation of CdTe when the particles are electrically excited in the presence of trace oxygen.

### Summary and Outlook

Lateral patterns of two different types of PDDA/CdTe multilayer films were prepared by a novel method combining electrophoretic deposition and layer-by-layer self-assembly. Using EFDLA, large color contrasts between adjacent pixels made up of different PDDA/CdTe films can be achieved in photoluminescence and electroluminescence. Although only dual-color patterns have been realized by EFDLA so far, there is, in principle, no limitation for the number of independent patterns to be formed on one common substrate. Since the same electrodes used during the deposition process can then be utilized to address (opto)electronically active pixels of nanocrystals, the realization of multicolor pixel arrays by the EFDLA method opens up an elegant way toward nanocrystal multicolor displays.

Detailed experimental results from SEM and fluorescence spectroscopy also prove that a voltage of 1.4 V is required to get 99% contrast between favorable deposition and unfavorable deposition on ITO. However, the QCM results indicate that a voltage of 0.6 V is enough to realize high selectivity on Au electrodes. This dramatically reduces the risk of electrochemical degradation of the deposited materials on the working electrode and makes the EFDLA method therefore attractive for fabricating multiple functional thin film sensors by laterally combining different types of sensory materials on a single sensor chip.

**Acknowledgment.** This work has been financially supported by the Bundesministerium für Bildung und Forschung (BMBF 03N8604 9) and the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 486 and the Gottfried-Wilhelm Leibniz award. We gratefully thank M. Dulkeith for taking the color images and C. Sönnichsen for his help with the EL experiments.

LA015599A

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