

# Electric Field Directed Layer-by-Layer Assembly of Highly Fluorescent CdTe Nanoparticles

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An electric field directed layer-by-layer assembly technique has been developed by combining electrophoretic deposition and the layer-by-layer self-assembly method. This technique is employed to realize spatially selective deposition of CdTe nanoparticles on electrodes of Indium-Tin Oxides (ITO). The fluorescence measurements prove that the selectivity of the film deposition increases against applied voltage and reaches 99 % when the voltage is 1.4 V. Upon further increase of the voltage, the selectivity slightly decreases. This decrease occurs because high voltage leads to degradation of CdTe particles and thus reduces fluorescence intensity of the resultant CdTe film. However, fluorescence investigation indicates that a spacer layer of polyelectrolyte complex between the ITO electrode and the CdTe film is useful to protect the CdTe from being destroyed under high voltages.

**Keywords:** CdTe Nanoparticles, Electric Field Directed Assembly, Lateral Structure, Layer-by-layer Self-assembly, Spatially Selective Deposition

The layer-by-layer (LbL) self-assembly technique based on electrostatic interaction has provided a unique way to fabricate ultrathin molecular assemblies and ample room to fully tailor the properties of the assemblies by combining different types of polyionic species into layered structures.<sup>1</sup> The simplicity of operation and versatility in the material choice make this technique very promising for fabricating devices such as biological sensors, electroluminescent devices, and photovoltaic devices.<sup>2</sup> Very recently the LbL self-assembly method was successfully combined with soft lithography to produce micropatterns that are potentially useful for fabrication of light-emitting pixels for monochrome displays.<sup>3,4</sup> However, realization of a multicomponent lateral structure consisting of more than two types of independent patterns remains a bottleneck for the LbL self-assembly method in applications such as multicolor displays as well as multiple functional sensors. Thus it is very meaningful to further develop the LbL self-assembly method to gain the ability to realize multicomponent lateral structures based on a spatially selective deposition from the point of view of both fundamental and application oriented research.

The key issue for realizing multicomponent lateral structures by the LbL self-assembly method is how to stop the film growth in one area and subsequently start another film deposition process in a different area effectively. It is well known that by applying an electric field, the deposition of charged species on an electrode can be

accelerated and decelerated.<sup>5</sup> This is the basis of the electrophoretic deposition technique. If the accelerating and decelerating effects are large enough, the start and stop of the film growth driven by electrostatic attraction can be realized on electrodes. Moreover, if a series of electrodes are placed on the same substrate and spatially separated, we will be able to produce a multicomponent lateral structure by defining the polarities on different electrodes. In light of this idea, an electrophoretic deposition technique<sup>5-7</sup> is combined with the LbL self-assembly method to realize effective control over self-assembled film growth and, consequently, to achieve a spatially selective deposition. We call this new technique *electric field directed layer-by-layer assembly* (EFDLA). Anionically charged strongly fluorescent CdTe nanoparticles and cationically charged poly(diallyldimethyl ammonium chloride) (PDDA) are employed to demonstrate the feasibility of this EFDLA technique.

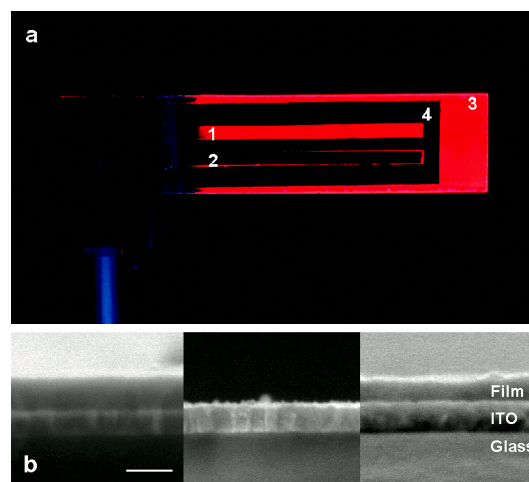
CdTe nanoparticles stabilized by thioglycolic acid were synthesized according to Ref.<sup>8</sup> Their average diameter was  $\sim 3.5$  nm determined by high-resolution transmission electron microscopy. The pH value of the CdTe particle solution was adjusted to  $7.8 \pm 0.2$ , which resulted in dissociation of the carboxylic group and gave rise to negative charges on the particle surface. Typical concentrations of the CdTe and PDDA solutions were  $1.3 \times 10^{-3}$  M ( $\text{Cd}^{2+}$ ) and  $5 \times 10^{-2}$  M (with respect to the repeat unit), respectively. Indium-tin oxide (ITO) glass with a sheet resistance of  $30 \Omega/\square$  was

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used as electrodes as well as substrate for film deposition. Two-electrode systems were adopted with the electrodes in either a face-to-face or a side-by-side arrangement. The electrode on which deposition takes place preferentially is denoted as the working electrode and the deposition on it is called favorable deposition. The other electrode on which the deposition cannot take place or becomes difficult is called the counterelectrode and the deposition that occurs there is called unfavorable deposition.

The EFDLA deposition procedure is quite similar to that for the traditional layer-by-layer self-assembly reported before<sup>9-11</sup> except that a certain dc voltage is applied during the assembling process. In the two-electrode systems, ITO electrodes were either fixed by 3 mm in the face-to-face manner or 1 mm distance in the side-by-side fashion. No difference with respect to the film quality or the effectiveness of the electric field was practically observed. Typically, the (PDDA/CdTe)\**n* film was prepared by alternately adsorbing CdTe particles and PDDA for 4 minutes under a voltage of 1.4 V followed by a 3-min washing procedure using Milli-Q water. The polarities on both the working electrode and the counterelectrode were defined in a way that the electric field always accelerated the assembling process on the working electrode and decelerated it on the counterelectrode. This means that the polarities on the two electrodes have to be switched back and forth each time the electrodes are transferred from one solution to the other.<sup>12</sup>

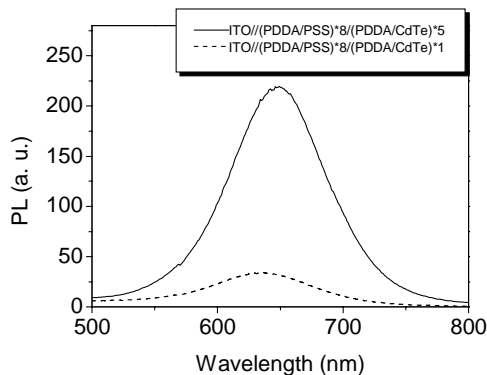
A fluorescence image of 40-bilayer CdTe and PDDA alternating films deposited by the EFDLA technique on a structured ITO substrate is shown in Figure 1a. The structured ITO substrate was obtained by chemically etching ITO glass through an adhesive tape mask and then using the complementary part of the mask as a resist against film growth in the bare glass area during subsequent film deposition. The applied voltage and deposition time for each layer of CdTe and PDDA were 1.4 V and 4 min, respectively. The working electrode exhibits strong red fluorescence, whereas the counterelectrode appears dark. Typically the outer area of the two electrodes is covered by the adhesive tape resist during sample preparation. Due to a small misalignment, a narrow gap between the electrode and the resist becomes available for the build-up of freely self-assembled CdTe film and it thus appears as a red line around the counterelectrode. Similarly, due to the presence of freely self-assembled CdTe films, the margin area of the substrate also appears red in the fluorescence image. The huge fluorescence contrast between the working and counterelectrodes clearly shows that the deposition of the CdTe particle film occurs exclusively on the working electrode. This conclusion is further supported by cross-sectional scanning electron microscope (SEM) measurements, as shown in Figure 1b. The total thickness of the freely self-assembled film is about 101 nm; the thickness of the film on the working electrode is about 146 nm. In contrast, there is hardly any visible film on the counter-



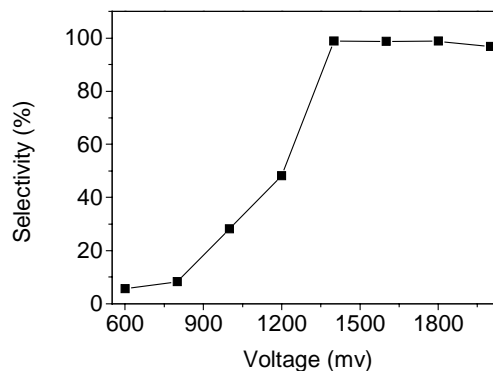
**Fig. 1.** (a) Fluorescence photograph of the (PDDA/CdTe)\*40 film deposited on one piece of rectangular glass with four different areas: 1, working electrode; 2, counter electrode; 3, margin; 4, bare glass area that was originally covered by a removable resist (adhesive tape) during the sample preparation. (b) Cross-sectional SEM images of area 1, 2 and 3 (left to right)

electrode. However, from the SEM results, it is still hard to tell if the film on the working electrode is really fabricated by alternating CdTe with PDDA or by continuously depositing CdTe particles themselves.

To clarify this mechanism, two types of films were deposited by the EFDLA technique on ITO working electrodes that were initially covered by a 6-bilayer PDDA/PSS film (PSS, polystyrenesulfonate,  $2 \times 10^{-2}$  M (concentration with respect to the repeat unit)). One of the film was a 5-bilayer PDDA/CdTe film fabricated by immersing both working and counterelectrodes alternately in PDDA and CdTe solutions for 4 min (film 1). The other type was a 1-bilayer PDDA/CdTe film prepared with a deposition time of 20 min in the CdTe solution (film 2). The fluorescence spectra of the two films were recorded for comparison. A strong photoluminescence (PL) emission peaking at 648 nm from film 1 can be observed in Figure 2. Film 2 presented much weaker fluorescence although the duration times for both films in the CdTe solution were the same. The huge fluorescence contrast proves that there are more CdTe particles loaded on film 1 than on film 2. This result indicates that film 1 is a PDDA/CdTe multilayer film constructed in layer-by-layer fashion, whereas film 2 is just one layer of CdTe nanoparticles with its amount being limited by adsorption saturation. This conclusion also explains why the thickness of the CdTe film on the working electrode is higher than that of the freely self-assembled film. Usually the surface coverage of nanoparticle layers formed by electrostatic interaction is not high enough to form a complete layer structure, whereas much denser packing can be achieved by



**Fig. 2.** Fluorescence spectra of film 1 (solid line) and film 2 (dashed line) prepared by the EFDLA technique. The duration times of both films in the CdTe solution were 20 min.



**Fig. 3.** Voltage-dependent selectivity between favorable and unfavorable depositions obtained from the (PDDA/CdTe)\*10 films fabricated by the EFDLA technique.

applying an electric field.<sup>11</sup> As a result, the film on the working electrode presents a larger thickness.

The effectiveness in controlling the start and stop of the PDDA/CdTe film deposition by the EFDLA technique is expressed by a selectivity ( $S_{\text{CdTe}}$ ) that is defined by the equation  $S_{\text{CdTe}} = (I_f - I_u)/(I_f + I_u)$ , where  $I_f$  and  $I_u$  are fluorescence intensities of the CdTe films obtained under favorable and unfavorable deposition, respectively. In general, the selectivity increases with increase of voltage or electric field and reaches 99 % at 1.4 V, as seen in Figure 3. The result is qualitatively not surprising because the increase of the external voltage (electric field) increases the accelerating and decelerating effects on the corresponding electrodes. As a result, the selectivity increases. Quantitatively the abrupt increase in selectivity with voltage is not yet understood.

A slight decrease in selectivity above 1.4 V indicates that the CdTe nanoparticles are degraded on the working electrode faster than on the counterelectrode. This degradation was systematically investigated by measuring the fluorescence of the CdTe films prepared by the conventional self-assembly method before and after the films were subject to different voltages. Two types of CdTe films were prepared. The first type of samples were (PDDA/CdTe)\*12 film directly deposited on ITO glass. The second type of samples were also (PDDA/CdTe)\*12 films but they were deposited on ITO electrodes that were first covered by a (PDDA/PSS)\*8 film. The ITO counterelectrodes with a bare surface or covered with adhesive tape were adopted. In different combinations, CdTe film covered ITO electrodes and counterelectrodes were fixed by a 3 mm distance in a face-to-face manner. The positive pole of the dc power supply was connected to the CdTe film covered electrode. The fluorescence intensity of the CdTe films was measured each time after the electrodes were immersed 5 min in pure water or 0.1-M KCl solution under a stepwise increased voltage; the data are tabulated in Table 1.

In pure water the fluorescence of the first type of CdTe film loses more than a half of its initial intensity by using bare ITO as counterelectrode at 1.2 V. However, by using a counterelectrode sealed with adhesive tape, the fluorescence of this CdTe film only loses a bit more than a quarter of its initial fluorescence intensity even when the applied voltage reaches 2 V. This observation clearly proves that CdTe nanoparticles can easily be oxidized at high voltages when a bare counterelectrode is used. By using 0.1-M KCl instead of pure water, a similar decay of fluorescence against voltage is observed (Table 1). However, regardless of whether water or KCl solution is used, the retained fluorescence intensity of the second type of CdTe film is higher than that obtained from the first type of CdTe film by using the bare counterelectrode. Under an optimized voltage of 1.4 V for the EFDLA deposition of CdTe particles, the retained fluorescence intensity improves by at least a factor of 2. This result proves that the spacer layer can protect the CdTe nanoparticles from electrochemical degradation. Experimental results of cyclic voltammetry show an anodic shoulder at around 0.7 V and maxima around 1.2 V [vs. Ag/AgCl (3-M KCl) electrode] from the CdTe nanoparticles. Detailed electrochemical properties of the CdTe nanoparticles will be published elsewhere.<sup>13</sup> Here we point out that the magnitude of the voltage for controlling the deposition process depends very much on the system. It has been proven that only hundreds of milli-volts are sufficient to obtain a densely packed layer of Au colloids.<sup>6</sup> In such a case, unwanted electrochemical reactions can easily be avoided.

In conclusion, by choosing negatively charged CdTe nanoparticles and positively charged PDDA as model materials, we have successfully realized the spatially selective deposition of a layer-by-layer assembled film directed by an electric field. The SEM results together with fluorescence results indicate that by using the EFDLA technique, multilayer deposition can be achieved.

Table 1, Voltage-dependent fluorescence of freely self-assembled (PDDA/CdTe)\*12 films on ITO before and after being treated under different voltages in pure water or 0.1-M KCl solution. All the fluorescence intensities are normalized with respect to the original fluorescence intensities of the CdTe films<sup>a</sup>

Voltage (mV)	Fluorescence (% water)			Fluorescence (% KCl aq)		
	S + CdTe	B + CdTeP	B + CdTe	S + CdTe	B + CdTeP	B + CdTe
0	100	100	100	100	100	100
600	98.4	98.8	98.7	95.2	96.4	92.6
800	96.0	89.6	91.4	86.9	90.1	83.8
1000	91.5	76.5	77.1	81.8	76.5	67.8
1200	86.4	58.2	41.9	72.5	55.9	45.6
1400	82.5	35.8	9.4	65.4	27.8	13.9
1600	80.3	12.9	0.6	57.1	7.6	0.7
1800	76.7	0.9		53.2	0.3	
2000	72.8			45.6		

<sup>a</sup> S, sealed counterelectrode; B, bare counterelectrode; CdTe, CdTe film deposited directly on ITO working electrode; CdTeP, there is a (PSS/PDDA)\*8 precursor film between the CdTe film and ITO working electrode.

This enables the EFDLA technique to take over the existing advantages of the layer-by-layer self-assembly method. Most importantly, the powerful and unique features of the EFDLA technique are very suitable for fabricating sophisticated structures in both lateral and normal directions of the film for most ionic self-assembling systems.

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