

## Support information

### 1. Preparation, Characterization and Optical properties of the negatively charged CdSe nanoparticles

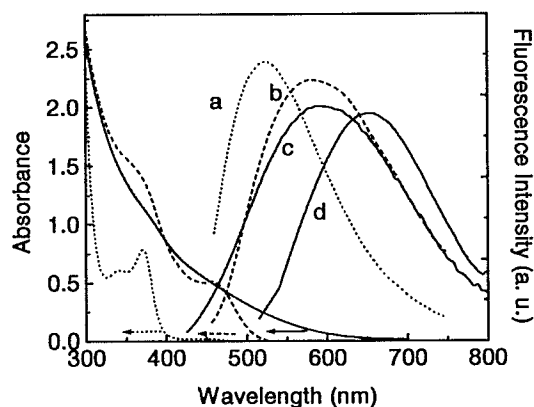
The CdSe particles were prepared in the following steps. First, 100 ml of a mixed solution containing  $10^{-3}$  M  $\text{Cd}(\text{ClO}_4)_2$  and  $10^{-3}$  M thiolactic acid was prepared in a three-neck flask. After the pH value was adjusted to 11 by using 0.1 M sodium hydroxide solution, the mixture in the flask was purged with Argon for 30 minutes. Then  $\text{H}_2\text{Se}$  gas, which was collected from the reaction of  $\text{Al}_2\text{Se}_3$  with diluted phosphoric acid or water, was injected into the container using a syringe. A yellow color appeared shortly after the gas was injected, at the same time the solution showed very strong fluorescence. As more gas was introduced into the reactor, the color of the solution became red, and the fluorescence intensity decreased. Ten minutes after 1 ml  $\sim$  3.3 ml  $\text{H}_2\text{Se}$  was introduced, 0.5  $\sim$  1.2 ml  $10^{-1}$  M  $\text{Cd}(\text{ClO}_4)_2$  was injected into the mixture and the pH value of the solution decreased. When the pH was adjusted to 9 again, the strong fluorescence reappeared. The solution was purged again with Argon for 20 minutes in order to remove the unreacted  $\text{H}_2\text{Se}$ . The final particle solution without any further purification showed very good stability, it was preserved in the refrigerator for 10 months with no precipitation emerging.

The size of CdSe particles was controlled by varying the feed molar ratio between  $\text{Cd}^{2+}$  and  $\text{H}_2\text{Se}$  in the presence of thiolactic acid. The thiol groups from the thiolactic acid can combine on the surface of the particle after the formation of CdSe particles, which produces a shell of CdS around a CdSe core. Under high-resolution TEM ( Philips CM 200 FEG transmission electron microscope operating at 200 kV ), the core-shell particles are roughly round in shape. The average diameter of the particles is 4.9 nm with a standard deviation of 1.3 nm. The molar ratio of Cd:Se:S in the particle sample which was used for all electroluminescence experiments was measured as 53.6:18.9:27.4 by EDAX (Energy dispersive analysis of X-ray was performed with the aid of an EDAX DX4 spectrometer). A diameter of 3.7 nm for the CdSe core and a width of 0.6 nm for the CdS shell are calculated using the assumption that a complete layer structure of CdS was formed on the surface of a spherical CdSe particle.

By using the size selective precipitation technique,<sup>26</sup> several small fractions were obtained from the originally prepared particles. The absorption and fluorescence spectra of the original particle solution together with that of the two fractions are shown in Fig 1S. When comparing the absorption spectra of fraction I and II with that of the original solution, a pronounced transition at 457 nm and a shoulder at 370 nm appear in the absorption spectrum of fraction I. A more pronounced transition at 371 nm is present in the absorption spectrum of fraction II. If the peak at 457 nm of fraction I is attributed to the first electronic transition of the CdSe particle, then by comparison to literature data<sup>26</sup> an average particle size of approx. 1.6 nm for the CdSe cores is estimated. A much smaller particle size would be obtained for the fraction II from the absorption maximum at 371 nm. Therefore, fraction II was

suspected to consist of small clusters mainly formed from cadmium ions and thiolactic acid.

Nevertheless, the size distribution is significantly narrowed for both fractions compared to the original CdSe solution. However, all these particle solutions still present a very broad and red-shifted emission. This suggests that the emission is not due to the  $S_1-S_0$  transition of the particle but mainly results from trap sites of different depths. Detail studies on the CdSe nanoparticles capped with different thiols have proved the thiol surface coverage is far from complete passivation.<sup>34</sup> For the thiolactic acid stabilized CdSe particles, the steric hindrance from the methyl group of the thiolactic acid will decrease the thiol surface coverage. Therefore, thiolactic acid capped CdSe present a broad lower energy band emission from the trap state localized on the particle surface. Two fluorescence spectra recorded from the original CdSe solution are shown as c and d in Fig 1S. The excitation positions are 400 nm and 500 nm, respectively. The shift of the fluorescence along with the excitation position also indicates that the original CdSe sample has a large particle size distribution. Because of this large particle size distribution and the existence of surface defects, the CdSe sample presents a broad photoluminescence that looks nearly white in color.



**Figure 1S.** Absorption and fluorescence spectra of the originally prepared CdSe solution (solid lines) together with that recorded from two fractions (fraction I, dashed lines; fraction II, dot lines) which were obtained by size selective precipitation. The excitation position is 360 nm for the fluorescence spectra of the two fractions, 400 nm (left fluorescence spectrum in solid line, c) and 500 nm (right one in solid line, d) for the originally prepared CdSe solution, respectively.

### 2. Preparation of structurally different films by self-assembly method

The pre-PPV, a positively charged polyelectrolyte, was synthesized according to literature.<sup>1a</sup> Its concentration was calculated by weighing the solid powder obtained by freeze-drying a certain volume of pre-PPV solution. The concentrations of PEI, PAH and the precursor of PPV solutions were  $10^{-2}$  M,  $10^{-2}$  M and  $3.8 \cdot 10^{-2}$  M respectively

(according to the repeat units).

The substrate (glass, ITO or Si ) was washed with Milli-Q water several times after it was cleaned by immersion in a mixed solution ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  of 1:1:5) for 20 minutes at 80 °C, then was dipped into PEI solution for 30 minutes. After being washed with water for several times, it was immersed into CdSe or PSS solution for 20 minutes. During this process, the negatively charged species were adsorbed onto the substrate and thus the substrate's surface became negatively charged. Again after being washed, the substrate was dipped into a solution of PAH or pre-PPV. After 20 minutes another layer of positively charged polyelectrolytes was adsorbed on top of the negatively charged layer and the sign of surface charge was reversed. By repeatedly dipping the PEI covered substrate into the PSS or CdSe, and pre-PPV or PAH solution for definite times, films with defined structures were obtained.