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PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE OF CdSe AND CdTe NANOPARTICLES

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CdSe and CdTe nanoparticles are prepared by treating aqueous solutions of Cd^{2+} ions with H_2Se and NaHTe respectively in the presence of different thiols. Due to the existence of trap sites on the CdSe nanoparticle surface, a broad emission that looks nearly white in color is presented. Bandgap photoluminescence is however obtained from the CdTe nanoparticles. The particle size of CdTe as well as the color of its photoluminescence can be tuned simply by refluxing the CdTe colloidal solution. By self-assembly method, the CdSe and the CdTe nanoparticles can be inserted into ultrathin films in combination with different kinds of polyelectrolytes. The electroluminescence results reveal that the electroluminescence of the self-assembled particle/PAH film devices resembles the photoluminescence of the particles. Thus, electroluminescence in different colors is produced, i.e., yellowish white light from (CdSe/PPV)*n and (CdSe/PAH)*n devices, orange and red light from the (CdTe/PAH)*n devices which contain CdTe particles varying in size. It is also proved that when particles are combined with PPV in an alternate way by self-assembly method, PPV works as a charge transportation layer. As a result, a much lower external voltage is needed to turn on the (CdSe/PPV)*n device than that for the (CdSe/PAH)*n device which has the same number of double-layers as the former one. Moreover, the CdSe nanoparticles also present a special stabilizing effect on the electroluminescence of PPV in (CdSe/PAH)*n/(PSS/PPV)*n two-*layer* composite film devices. This is because of the CdSe nanoparticle being able to consume the oxygen that exists in between the electrodes under a proper polarity. Hence in the subsequent measurements, the electroluminescence of PPV from the (CdSe/PAH)*n/(PSS/PPV)*n two-*layer* composite film devices is as stable as that from a single-*layer* (PSS/PPV)*n device when the later was operated in Helium after being stored in vacuum.

1. INTRODUCTION

Many types of materials, such as organic dyes[1], conjugated polymers[2-7], rare earth

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elements[8] and porous silicon[9], etc., have been used as emitting materials to prepare electroluminescence devices. Recently, the use of II-VI inorganic semiconductor nanoparticles in combination with polymers in the manufacture of LEDs has been reported[10-12]. As a new type of material, semiconductor nanoparticles present very unique properties. Because of the quantum size effect the absorption and photoluminescence spectra of the Q-size semiconductor particles can easily be tuned by varying the particle size. Additionally, the photoluminescence efficiency and the stability of the nanoparticles can be greatly improved by modifying the particle surface[13-15]. These advantages make the nanoparticle materials an ideal candidate for use in electroluminescence applications.

A well established self-assembly (SA) method was adopted to combine the CdSe and CdTe nanoparticles with different types of materials in the preparation of the nanoparticle LEDs. The SA method constructs ultrathin molecular films by sequentially adsorbing oppositely charged polyelectrolytes from aqueous solution[3,16-17]. It has been demonstrated that by this method materials such as conductive polymers, organic dyes and semiconductor nanoparticles can be assembled into ultrathin films. This offers the possibility to combine different materials into a composite film and thus to build up two- or three-*layer* structured LEDs.

In this paper, photoluminescence of CdSe and CdTe particles and electroluminescence (El) of the self-assembled nanoparticle film devices are reported.

2. EXPERIMENTAL SECTION

2.1. Preparation of CdSe and CdTe nanoparticles

In principle, the CdSe and CdTe nanoparticles were prepared by treating aqueous solutions of Cd^{2+} ions with H_2Se gas and NaHTe respectively in the presence of different thiols. During this process, the thiols served as stabilizing agent. Thiolactic acid and thiolglycolic acid were used respectively for the preparation of CdSe and CdTe. After the formation of the particles, the thiol group was bound at the surface of the particle and left the carboxylic group outside. Because of the deprotonation of the acid group, the surface of the particles become negatively charged at high pH values. This makes it possible to combine the nanoparticles in ultrathin molecular films by the self-assembly method. More details about the preparation of these two types of particles have been reported elsewhere[12,18].

2.2. Preparation of self-assembled CdSe and CdTe nanoparticle films

Poly(ethylenimine) (PEI) was used as the first layer, as reported elsewhere[19], for the preparation of all SA films in this paper. Poly(allylaminehydrochloride) (PAH) and the precursor of poly(*p*-phenylenevinylene) (PPV) as positively charged species and the CdSe, CdTe nanoparticles and PSS as negatively charged species were used for the preparation of the self-assembled films. Glass, ITO (indium tin oxide with 63 Ω/□) and silicon wafers were selected as substrates for different experimental purposes. By repeatedly dipping the PEI covered substrates into the PSS, CdSe or CdTe aqueous solutions and pre-PPV or PAH solutions for definite times, films with defined structures were obtained. The pre-PPV in the films was converted into PPV by heating treatment at 130 °C under 10^{-5} bar vacuum for 11 hours.

2.3. Preparation of self-assembled CdSe and CdTe nanoparticles film LEDs

All electroluminescent devices were fabricated by integrating the SA films in between the ITO and Al electrodes. A round shaped Al electrode, 3 mm in diameter and 115±15 nm in thickness, was prepared by vacuum evaporation. Electroluminescence spectra were measured by a spectrometer consisting of a monochromator (SP275, Acton) and a thermoelectrically cooled CCD camera (S&I) via an optical fiber. No collimating optics was used.

3. RESULTS AND DISCUSSION

3.1. CdSe nanoparticles

In the preparation of CdSe, thiolactic acid was used as the stabilizing agent. 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.

By using the size selective precipitation technique, several small fractions were obtained from the originally prepared particles. The absorption and photoluminescence spectra of the original particle solution together with that of the two fractions are shown in Fig 1. 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[13] an average particle size of approximately 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.

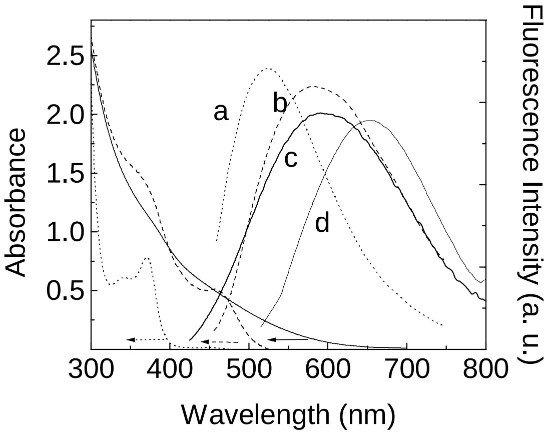

Figure 1. Absorption and fluorescence spectra of the originally prepared CdSe solution (solid lines) together with that recorded from two fractions (fraction I, dashed lines; fraction II, dot lines) which were obtained by size selective precipitation. The excitation position is 360 nm for the fluorescence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

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 that the thiol surface coverage is far from complete passivation[20]. Moreover, 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 photoluminescence spectra recorded from the original CdSe solution are shown as *c* and *d* in Fig 1. The excitation positions are 400 nm and 500 nm, respectively. The shift of the photoluminescence along with the excitation position also indicates that the original CdSe sample has a large particle size distribution. It is due to the large particle size distribution and the existence of surface defects that causes the CdSe samples to present a broad photoluminescence that looks nearly white in color.

The originally prepared CdTe nanoparticles were used for the preparation of SA CdTe nanoparticle films. The absorption spectra of (CdSe/PAH)*n films with different numbers of double-layers are presented in Fig 2. The absorbance measured at 300 nm, 350 nm and 400 nm is linearly increasing with the number of dipping cycles. This indicates that equal amounts of CdSe particles is adsorbed after each dipping cycle.

The (CdSe/PAH)*n multilayer films deposited on silicon wafer were characterized by X-ray reflectivity. A box model was used to fit the experimental reflectivity curves. A total film thickness of 34.9 nm and a surface roughness of 2.7 nm were obtained for the 12 double-layer of CdSe/PAH film. The volume fraction of the CdSe particles in the CdSe/PAH film was estimated to be 23 % using the electron densities of the CdSe and PAH which are extracted by fitting the experimental reflectivity. The results of the X-reflectivity from CdSe/PAH films with different numbers of double-layers indicate that the surface roughness of the film is relatively independent of the film thickness.

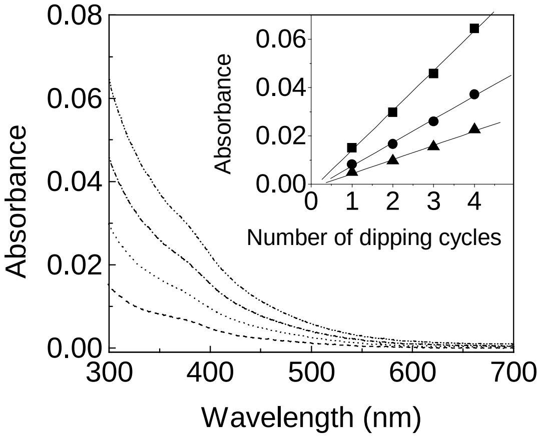

Figure 2. Absorption spectra of 1, 2, 3 and 4 double-layers CdSe/PAH self-assembled films. Insert: Absorbance at 300 nm, 350 nm and 400 nm of (CdSe/PAH)*n films against the number of dipping cycles.

3.2. CdTe nanoparticles

The CdTe nano-colloidal solutions were prepared using the reaction between Cd^{2+} and NaHTe in the presence of thioglycolic acid. The reaction took place very fast and changed the color of the mixture to orange. No photoluminescence was observed with the crude solution. Under reflux the photoluminescence of the solution appeared and could be tuned by prolonging the refluxing time. The solution was refluxed under air and the aliquots were taken at different times to monitor the cluster growth. After CdTe nanocrystals reached a certain size, 1/4 fractions of the refluxed solution were taken with remainder continuing under reflux. The CdTe colloidal solution was thus divided into 4 fractions (called below sample *I, II, III* and *IV*).

The evolution of absorption and photoluminescence spectra of the CdTe colloidal solution during the refluxing process is shown in Fig. 3. The colloidal solution gives a non-structured absorption spectrum with a long tail extending to 650 nm before reflux and no photoluminescence was observed. After it was boiled for several minutes, a clear shoulder at 490 nm appears and the long-wavelength wing of the absorption spectrum become much steeper than that of the original solution. Meanwhile, the solution showed a strong single band emission with the maximum around 535 nm. This near absorption onset emission (the so-called excitonic emission) shifted from 535 nm to 650 nm after 27 h of continuous reflux. In addition, the emission band broadens but the maximum remains near the absorption onset as shown in Fig 3b.

As discussed in Ref. [19], thermodynamically stable clusters, the precursor of CdTe nanocrystals, are formed at room temperature by the reaction between Cd^{2+} and NaHTe in the presence of thioglycolic acid. CdTe nanocrystals are then formed at high temperature during refluxing of this colloidal solution. The appearance of the narrow band emission near the absorption onset and the changes of the absorption spectrum of the colloidal solution shortly after reflux demonstrate this drastic change of the clusters' structure. Further evolution of the absorption spectrum was caused by increments in the CdTe crystal size, which has been demonstrated by TEM.

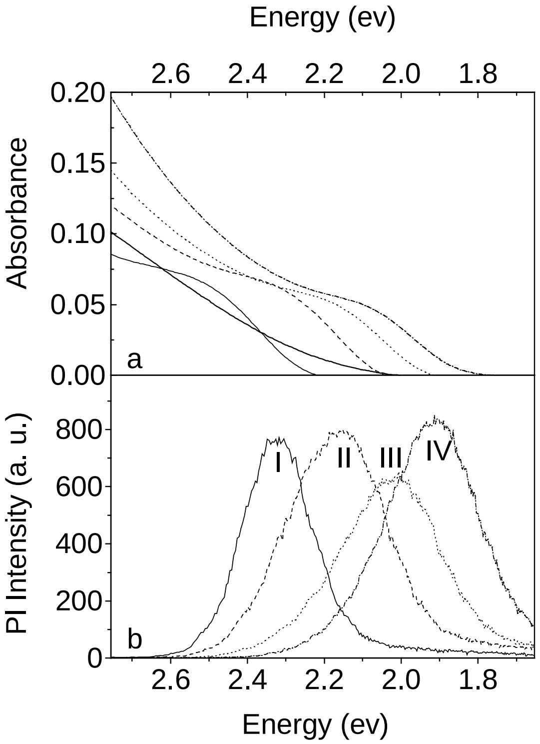

Figure 3. The evolution of absorption spectra (Frame a) and photoluminescence spectra (Frame b) of CdTe particle solution during the refluxing process. The absorption spectrum in heavy solid line was recorded from the crude CdTe colloid solution before reflux.

CdTe and PAH alternate multilayer self-assembled films were fabricated using the different size CdTe particles. It was found that the film formation strongly depends on the pH value of the CdTe particle solutions. Research on this is still on the way. By sandwiching the (CdTe/PAH)*n in between ITO and Al electrodes, the LEDs were prepared.

4. ELECTROLUMINESCENCE OF THE SA PARTICLE FILM LEDs

4.1. Electroluminescence of self-assembled CdSe/PAH and CdSe/PPV film devices

The I-V curve of an ITO//PEI(CdSe/PPV)*20//Al and the El spectrum recorded from it are shown in Fig 4. The emitting light looks nearly white in color. By comparing the electroluminescence spectrum with the photoluminescence spectra of the CdSe solution and (CdSe/PAH)*n film it was proved that the electroluminescence of the ITO//PEI(CdSe/PPV)*20//Al devices comes from the CdSe. Similar El spectra were also recorded from the ITO//PEI(CdSe/PAH)*20//Al device. The difference between the ITO//PEI(CdSe/PPV)*n//Al and the ITO//PEI(CdSe/PAH)*n//Al devices though both had the same number of double-layers a much higher (~ 10 V) voltage was required to turn on the CdSe/PAH multilayer film device. This indicates that in the former case charge carrier injection occurs mainly via PPV. Therefore, the injection of charge carriers at low voltage is very efficient. In the latter case a higher turn-on voltage is needed either to inject charge carriers in the non-conducting PAH or into the CdSe particles at a larger distance from the electrode. At the moment, these two alternatives can not be distinguished. However, it can be concluded that PPV works as transportation layer in case of (CdSe/PPV)*20 devices. This is also supported by the experimental results that the electroluminescence comes from CdSe particles rather than PPV when they are alternately combined.

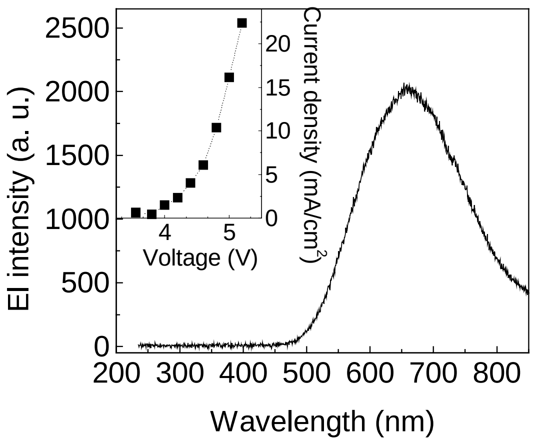

Figure 4. Electroluminescence spectrum of (CdSe/PPV)*20 SA film device. Insert: I-V characteristic of the device.

A red shift of the El emission was observed during the continuos operation of both CdSe/PPV and CdSe/PAH multilayer film devices. The changes in emission intensity and emission peak position of a 20 double-layer CdSe/PPV film device measured under a certain external voltage is shown in Fig 5. In the first several minutes, the emission intensity decreases dramatically. Meanwhile, the emission peak shows a fast red shift at a very early stage then followed by a slow process. The red shift of the CdSe emission implies that there are some new deep trap sites formed on the surface of the CdSe particles during the measurements. Since all the LEDs reported here were prepared and operated in air, there must be trace oxygen existing in between the electrodes. It has been proved

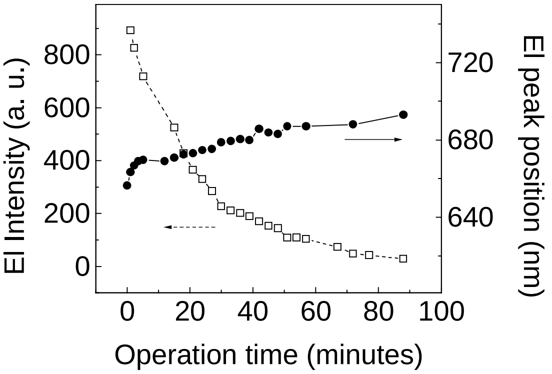

Figure 5. The changes in electroluminescence intensity and emission peak position during the in air operation.

that CdS nanoparticles can be oxidized in the presence of Oxygen when the particles are excited by illumination[16], this is so-called photo-oxidation. In case of electroluminescence, the appearance of light emitting from CdSe in the self-assembled film LEDs proves that the CdSe nanoparticles are excited under external potential. Thus the CdSe nanoparticles will experience the same process as the CdS does in the photo-oxidation process. The oxidation of CdSe will introduce more surface defects to the CdSe nanoparticles. As a result, the efficiency of the LED also decreases.

4.2. Electroluminescence of self-assembled CdTe/PAH film devices

The self-assembled CdTe nanoparticle film devices were constructed with such an ITO//PEI(CdTe/PAH)*n//Al structure. Different color emissions were obtained by using different size CdTe nanoparticles. The electroluminescence spectra recorded from SA CdTe/PAH film devices which contain CdTe nanoparticles varying in size are shown in Fig 6 a. The photoluminescence spectra of the devices are given in Fig 6 b. The electroluminescence of devices is quite similar to its photoluminescence except for a small red shift and broadening. However, the photoluminescence of the smaller CdTe particles in the device is much broader than that in aqueous solutions. This is because the particle size distribution of the CdTe particles in the film is larger than that in the aqueous solution. It was found that the stability of the smaller CdTe particles is very sensitive to pH, and the formation of CdTe/PAH SA film is also dependent on the pH. At the pH value selected for the preparation of the SA films, part of the small particles increase in size. As a result the smaller particles in the SA film show a much broader photoluminescence. More details on the pH effect of the CdTe/PAH formation and the CdTe particles' stability will be reported at a later date.

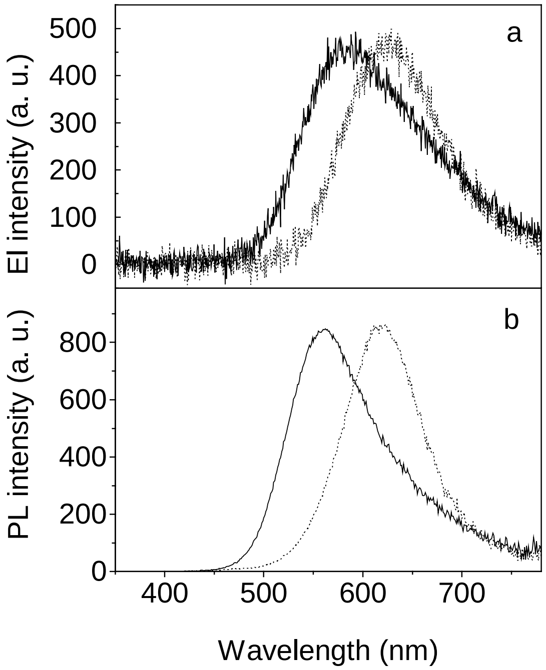

Figure 6. a, Electroluminescence (Frame a) and photoluminescence (Frame b) of 60 double-layers self-assembled CdTe/PAH film devices which contain CdTe particles varying in size. The electroluminescence spectra were recorded at room temperature in air.

5. THE SPECIAL STABILIZING EFFECT OF CdSe NANOPARTICLES ON El OF PPV

Devices with an ITO//PEI(CdSe/PAH)*10/(PSS/PPV)*n//Al structure were prepared by depositing ten double-layers of CdSe/PAH on top of ITO glass followed by ten double-layers of PSS/PPV and then evaporating Al on the top of the film. The electroluminescence spectra recorded from the above two-*layer* structure LED are shown in Fig 7.

When a freshly prepared sample was first operated under forward bias as shown in Fig 7 a*,* the typical PPV emission appeared at around 490 nm above 13 V. The appearance of this emission indicates that the recombination zone of charge carriers is located in the (PSS/PPV)*10 *layer*. PPV is a good hole conductor, hence electrons injected into it do not travel far from the cathode. Therefore with a polarity of Fig 7 a, electrons remain in the right part of the film. As a result, the recombination zone of the charge carriers is located in the (PSS/PPV)*10 *layer*.

As it can also be seen in Fig 7 a, the intensity of the PPV emission kept increasing until the voltage reached 15 V (the voltage-increasing rate is 0.5V/S), then it decreased. The device presented a very short lifetime which is in the same order as that of a (PPV/PSS)*n one-*layer* device. It was found that the PPV emission from a (PPV/PSS)*n one-*layer* device shifted to blue during the decline of the PPV emission. This indicates that the conjugation length of PPV is shortened during the operation due to the oxidation of PPV. Cumpston et *al* has proved by FTIR the oxidation process of PPV and found that this oxidation is one of the main reasons responsible for the failure of PPV LEDs[21-22].

It was also observed that once a fresh sample was first subjected to a forward bias, it never presented the emission from PPV again during subsequent measurements. After this operation, defects along the whole Al electrode were observed. The fast decline of the PPV emission and the appearance of the defects on the Al electrode proved that PPV was decomposed near the polymer/Al interface because of the oxidation reaction that occurred under current flow.

However, when a fresh sample was first subjected to a backward bias, as shown in Fig 7 b, a broad emission identical to the emission of the (CdSe/PAH)*20 device appeared at 12.5 V. Even under higher operating voltage, there is no emission observed from PPV. This proved that the recombination zone is located in the (CdSe/PAH)*10 *layer*. PPV is good hole-conductor. Holes injected from the Al electrode on the right side will quickly pass through the (PPV/PSS)*10 *layer* before the electrons injected from the

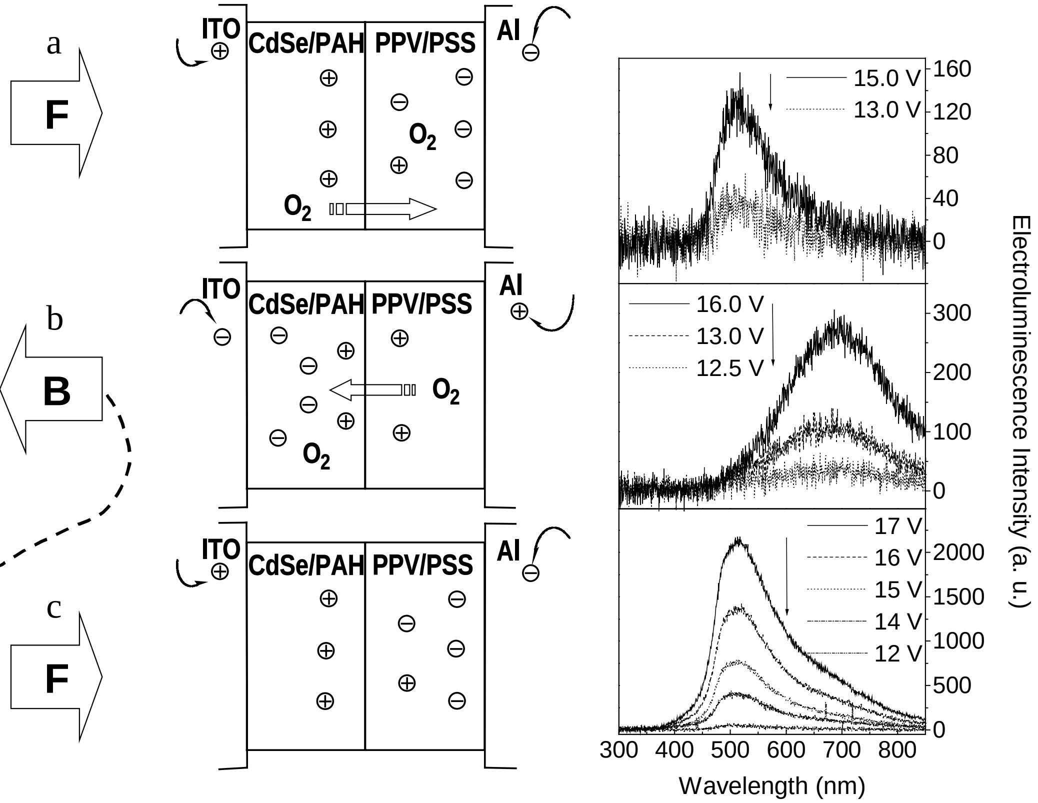

Figure 7. Schematic drawings of the structure of a ITO//PEI(CdSe/PAH)*10/(PSS/PPV)*10//Al *two-layer* composite film device (left). Electroluminescence spectra of the composite film devices (right) recorded at room temperature in air. The El spectra recorded from a fresh sample under forward bias are presented in the top frame. The El spectra recorded from a fresh sample under backward bias are presented in the middle frame and the El spectra recorded under forward bias after the device was operated under backward bias are shown in the bottom frame. Note that the intensity of the electroluminescence spectra shown in the right hand frames is comparable.

ITO electrode on the left side arrive at the (PPV/PSS)*10 *layer*, so the recombination takes place in the (CdSe/PAH)*10 *layer*. Thus, the particles are excited and oxidized rather than PPV. In this way all oxygen present in the film will be consumed, but with a less severe degradation of particles. After this backward bias operation, no visible defects on the Al electrode were observed.

When such a sample that was preconditioned under backward bias was subject to a forward bias, as shown in Fig 7 c, it presented a very intensive and stable emission from PPV. Its lifetime was nearly the same as that of the (PSS/PPV)*20 device when the later was operated in Helium after being stored in vacuum for 12 hours. This demonstrates that the oxygen presented in the film was consumed during the operation under backward bias. This allows an oxygen-free environment to be created within the film. For further oxidation, the oxygen has to diffuse from the outside, a process that is very slow. This picture is supported by the fact that the degradation pattern of the Al electrode on the two-*layer* device starts to decompose mainly from the border and not throughout the whole area.

6. SUMMARY AND CONCLUSIONS

Different kinds of self-assembled particle film LEDs have been constructed using PPV, CdSe, CdTe nanoparticles and other polyelectrolytes. Since the El of particle/PAH multilayer film devices resembles the photoluminescence of the nanoparticles, El in different colors was obtained by using different particle samples, i.e., nearly white light from (CdSe/PAH)*n and (CdSe/PAH)*n devices, orange and red light from (CdTe/PAH)*n devices which contain CdTe nanoparticles varying in size. When CdSe particles are combined with PPV in an alternate way, PPV works as a charge transportation layer. As a result a much lower external voltage is needed to turn on the (CdSe/PPV)*n device than that for the (CdSe/PAH)*n device with the same number of double-layers as the former one. In addition, the CdSe nanoparticles also present a special stabilizing effect on the El of PPV in (CdSe/PAH)*n/(PSS/PPV)*n two-*layer* composite film device. Because of the oxidation of PPV under the external potential, the (PPV/PSS)*n device presented short lifetimes. However, the lifetime of the PPV electroluminescence was enhanced when the (PSS/PPV)*n film was built on top of the (CdSe/PAH)*n SA film, but only after the composite film device was first operated under proper polarity. Then, during subsequent measurements the emission of PPV from the composite film device became as stable as that from a single-*layer* (PSS/PPV)*n device when the latter was operated in Helium after being stored in vacuum. We want to note that this stabilizing effect may provide a very general idea to protect the organic LEDs from being oxidized.

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