



A solvent/non-solvent system for achieving solution-processed multilayer organic light-emitting devices



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ABSTRACT

We developed a solvent/non-solvent system to fabricate the multilayer organic light-emitting devices (OLEDs) based on poly(N-vinylcarbazole) (PVK) by solution-process. This solvent system consists of both the solvent and non-solvent of PVK, in which fluorescent small molecules could be fully dissolved and directly spin-coated on top of the PVK layer; it could effectively avoid the redissolution of PVK during the spin-coating process of small molecules emitting layer. In the further investigation of this system, we also demonstrated the three-component solvent system, and found out that the third component, a less volatile solvent of PVK, was crucial for preparing a smoother interface between PVK and emitting layer. Compared with OLEDs through the vacuum deposition, the devices fabricated by solution-process from the solvent/non-solvent system showed comparable efficiency, which indicate that the solvent/non-solvent system can be used as an alternative process to prepare the polymer and small molecule multilayer devices through all-solution-process.

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1. Introduction

Since the first report of efficient organic light-emitting devices (OLEDs) by Tang et al. in 1987 [1], OLEDs have gained a lot of popularity among scientific researches for their potential applications in flat panel displays and solid state lighting. Solution process is highly regarded as the lowest-cost way to fabricate such devices, because it could spin-coat homogeneous and uniform layers with large area and, moreover, devices fabricated by this method exhibit as excellent performance as those prepared by vapor-deposition method [2]. Indeed, there have been some reports on solution-processed small-molecule OLEDs [3–6] and our group also has done much research on solution-processed OLEDs of small-molecule mixed-host structures [7–13]. However, things are quite different for OLEDs with structure of multilayer. The main reason is that the solution process itself causes redissolving problems between the layers, which makes us unable to take advantage of functions of a separate functional layer such as charge injection layer and charge-transporting layer. Much effort has been paid on the investigation of the fabrication of multilayer OLEDs by solution process. Fortunately, some groups succeeded by modifying the materials such as cross-linkable polymers [14,15], water/methanol-soluble copolymers [16,17], and others by using self-assemble methods [18] or by utilizing solvents with different properties [19,20]. S. R. Tseng [21,22] developed liquid buffer layer (BL) to fabricate multilayer OLEDs which was considered a general and reliable method to prepare arbitrary all-solution-

process OLEDs. Though there are lots of advantages of this method, it is not suitable to some small molecule materials with low T_g or decomposing at low temperature, because only at high annealing temperature can the BL be completely removed [23].

In this paper, we presented a solvent system, named solvent/non-solvent system, to fabricate multilayer OLEDs based on poly(N-vinylcarbazole) (PVK) by solution-process. The system consists of solvent and non-solvent of PVK which can fully dissolved fluorescent small molecules but will not destroy the PVK layer while spin-coating the small molecules emitting layer (EML). In this work there were two kinds of solvent/non-solvent systems: two-component system and three-component system. Compared with the two-component system, dichloroethane (DCE), which is less volatile than the other two components, was added to constitute the three-component system. Results showed that DCE is crucial for preparing smoother films from our solvent system. Comparable performance of the devices to those prepared by vacuum deposition indicates that our system is feasible.

2. Experiment

In this work, we use PVK as hole transporting layer (HTL), the EML is a blend of N,N'-bis-(3-Naphthyl)-N,N'-biphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) and tris-(8-hydroxyquinoline)aluminum (Alq₃). When preparing these bilayer films, the solvent/non-solvent system was used at an optimized proportion: the two-component system consists of 70% (V/V) of chloroform and 30% (V/V) of hexane, and three-component system of 60% (V/V) of chloroform, 30% (V/V) of hexane and 10% (V/V) of 1, 2-dichloroethane (DCE). The PVK layer was first spin-coated from chlorobenzene solution at a concentration of 12 mg/ml and a speed of

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3000 rpm, and then baked at 80 °C in vacuum for 30 min. Spin-rinsing procedure was involved to fabricate PVK/EML bilayer [24]. After spin-rinsing by the neat solvent system at 1000 rpm to remove the remaining soluble part of PVK, EML was spin-coated from the solvent system solutions directly on top of the PVK layer at a speed of 1000 rpm, and then annealed at 80 °C in vacuum for 30 min. The morphology of the films was measured by atomic force microscopy (AFM, model SOLVER P47 from NT-MDT, Moscow).

After PVK/EML film was prepared, 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), LiF and Al were vacuum deposited in sequence with thicknesses of 30 nm, 1 nm, and 150 nm, respectively. For the controlled devices, after the PVK layer was prepared, the neat solvent system was spin-coated on it and then baked at 80 °C in vacuum for 30 min, at last the ITO glass coated with PVK layer was transferred into the deposition chamber. The blended EML was co-evaporated to give the thickness of 40 nm, the same to that prepared by solution process. The functional layers of the vapor-deposited device are the same with the solution-processed ones. Thicknesses of the deposited layers and the evaporation speed of the organic molecular materials were monitored by quartz oscillator. Current–voltage–luminance (J–V–L) curves were performed on Keithley 2602. Ellipsometer was used to measure the thickness of the solution-processed films.

3. Results and discussion

3.1. Fabrication of PVK/EML bilayer

To prepare bilayer by all-solution-process, we should make sure that the first layer could not be destroyed while spin-coating the second one. We compared the ultimate thickness of PVK films after different kinds of solvents were spin-coated on. From Table 1, it was easy to conclude that the PVK was almost completely dissolved in solvents like chloroform, toluene, and chlorobenzene. However, only partial PVK was dissolved when either of our solvent systems was used. We also tested whether there was any change on PVK thickness when the spin-rinsing process was done for the second time (the second time was conducted directly after the first time was finished without further annealing.). In Table 2, the thickness of PVK films showed nearly no difference between them, indicating that when EML was spin-coated after the spin-rinsing procedure, the PVK layer would not be destroyed.

The above results could be explained by the dissolving mechanism of polymers. Polymers can be dissolved well in a solvent if its solubility parameter (δ) is approximately the same as that of the polymer or they have the same polarity. According to the equation expressed as follows [25]:

$$\delta_2 = \frac{\rho \sum F_i}{M_0} \tag{1}$$

where ρ is the density of a polymer, M_0 is the molecular weight of the repeating unit of the polymer, and F is the molar-attraction constant of the functional group. The solubility parameter of PVK is calculated to be 20.1 (J/cm³)^{1/2}, very close to that of chloroform and chlorobenzene, whose solubility parameters are 19 and 19.4 (J/cm³)^{1/2} respectively. Therefore they can dissolve PVK well. We also noticed that toluene can dissolve PVK as well although its δ is smaller than PVK. This

Table 1
The dissolving extent of PVK films in different kinds of solvents.

Prime thickness of PVK	CHCl ₃ chlorobenze toluene			CHCl ₃ :hexane (70%:30%)	CHCl ₃ :hexane:DCE (60%:30%:10%)
	52 nm	0 nm	0 nm	0 nm	43 nm

*PVK was spin-coated at 2000 rpm from chlorobenze solutions.

Table 2
The dissolving extent of PVK after the second time of spin-rinsing of neat solvent.

The prime thickness of PVK	CHCl ₃ :hexane (70%:30%)		CHCl ₃ :hexane:DCE (60%:30%:10%)	
	First time	Second time	First time	Second time
52 nm	43 nm	42.8 nm	39 nm	38.6 nm

*The second time was immediately conducted when the first one was done.

phenomenon happened mainly because they share the similar polarity due to their aromatic groups.

For the mixed-solvent which composes two or more components, its solubility parameter can be obtained according to the following equation:

$$\delta_{mix} = \delta_1\varphi_1 + \delta_2\varphi_2 + \dots + \delta_n\varphi_n \tag{2}$$

where δ_n and φ_n represent the solubility parameter and volume portion of component n . The solubility parameter of the two-component system and three-component system are calculated to be 17.7 and 17.6 (J/cm³)^{1/2} respectively, smaller compared to that of PVK. But from Table 1, we could see that these solvent systems still dissolved some PVK. This may be because that in the solvent system, the solvent effect is weaker than neat chloroform for some parts of the chloroform were replaced by hexane to form the solvent/non-solvent system. However, the main part of the system remains chloroform, so even though the solvent effect is reduced, it can still dissolve PVK, but the extent is not as serious as neat chloroform, as has been demonstrated in Table 1.

Though both of our solvent systems dissolve very little PVK, there are some differences on the topology of the PVK after spin-rinsing by

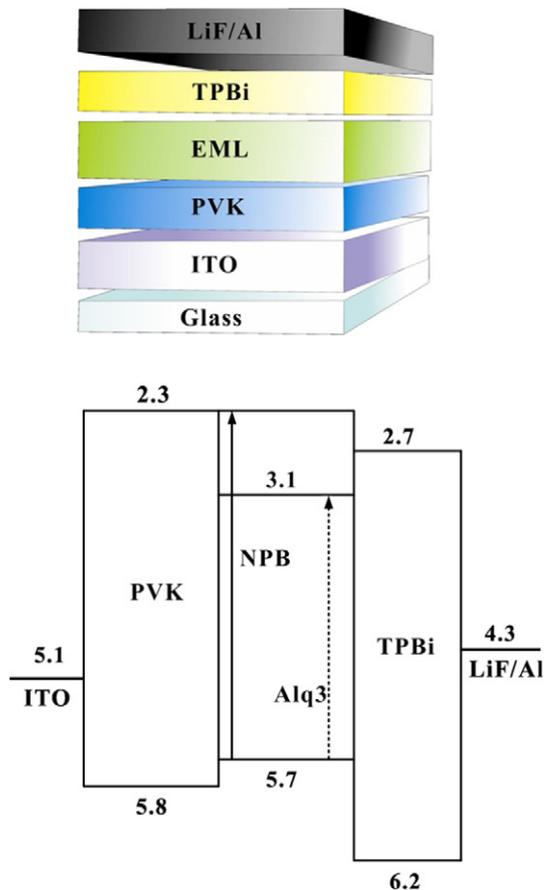


Fig. 1. Structures of the device and energy levels of the materials used.

the two systems. Fig. 2(a) showed AFM images of PVK film after the two-component system was spin-coated on, the Alq₃ film spin-coated from the two-component system and the PVK/Alq₃ bilayer prepared by two-component system were showed in Fig. 2(b) and (c). The root mean square (RMS) of (a), (b), and (c) is 5.4 nm, 1.1 nm and 3.2 nm, respectively. It was easy to find that lots of deep pinholes existed in the films in Fig. 2.

These pinholes revealed that there were some disadvantages with the two-component system. A possible explanation can be elucidated in Fig. 3. The volatility of chloroform (boiling point (b. p.), 61 °C) and hexane (b. p., 69 °C) is almost the same because of their approximate boiling point which measures the volatility of a solvent. When spin-coated, they evaporated simultaneously nearly at the same speed. Moreover, they did not interfere with each other while evaporating. As a result, PVK was dissolved away where chloroform flew over and then holes formed, while no changes happened where hexane flew over because it is a non-solvent to PVK, thus leading to large RMS of PVK films after the spin-rinsing procedure by two-component system.

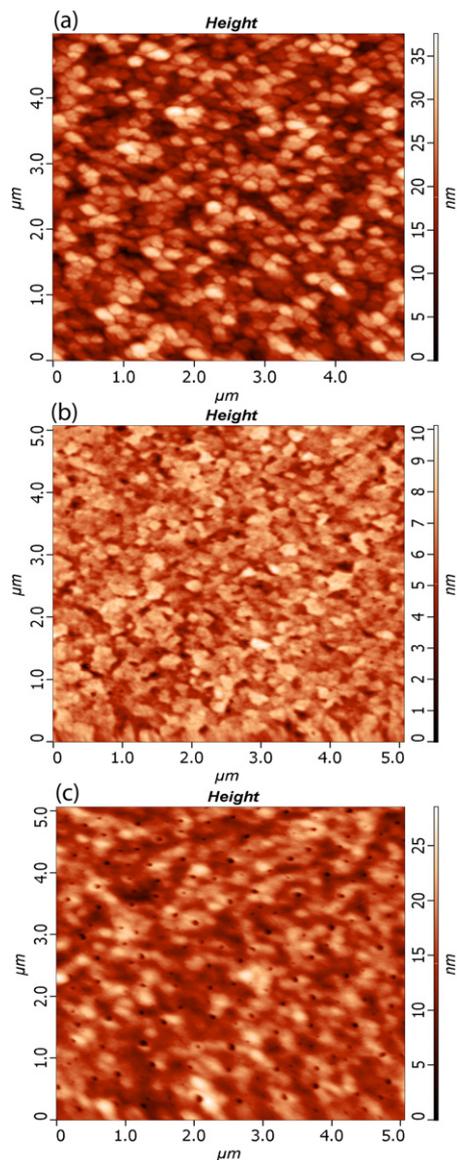


Fig. 2. (a) AFM images of PVK after two-component solvent system spin-coated on (b) AFM images of Alq₃ spin-coated from two-component solvent system solution (c) AFM of PVK/Alq₃ heterojunction layers by two-component solvent system.

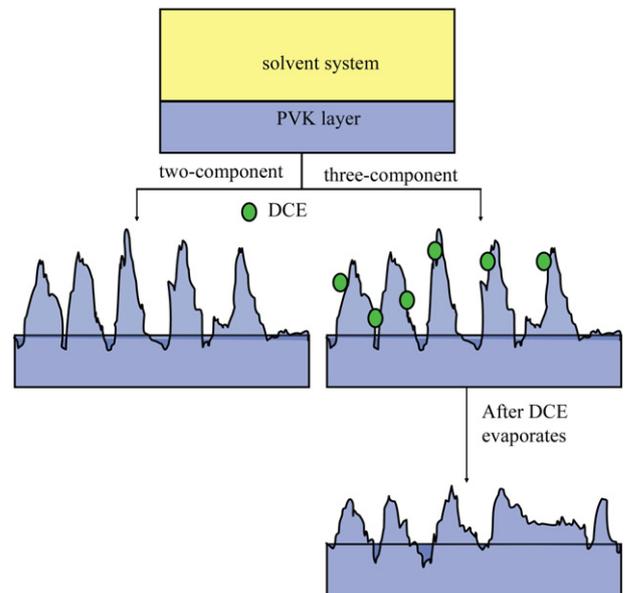


Fig. 3. Descriptions of the dissolving procedure during that the neat solvent was spin-coated on (open circular represents the solvent and the solid one non-solvent). When the double-mixed-solvent was spin-coated on, the solvent dissolved PVK and left holes after it, while the non-solvent had no effect on the films and the PVK blossomed up form the films. After DCE was added, it could dissolve the pointed PVK and level the film surface.

To improve the quality of PVK films, another solvent, DCE, which can dissolve PVK and has a higher boiling point (b. p., 83.5 °C) was added into the system. AFM images were shown in Fig. 4. Fig. 4(a) was the PVK film after the three-component system was spin-coated on, the Alq₃ film spin-coated from the three-component system and the PVK/Alq₃ bilayer prepared by three-component system were showed in Fig. 4(b) and (c). The RMS is 0.75 nm, 0.8 nm and 2.3 nm for (a), (b), and (c) respectively. It indicated that after DCE was added, the PVK films became smoother. This may be mainly attributed to the DCE component (the procedure also shown in Fig. 3). The less volatile DCE evaporated slower than chloroform and hexane when spin-coated, so it can dissolve the highlighted PVK left over by chloroform and hexane, and consequently smoothed the surface of PVK films.

3.2. Device characterization

As discussed above, three-component solvent system could form better thin films than the two-component solvent system. Therefore, we fabricated a series of OLEDs based on PVK/EML bilayer. The typical device structure was shown in Fig. 1 and the fabrication procedure together with the measurement methods were described in Section 2. From Fig. 5 where characteristics of the devices were shown, it can be seen that the performance of the device based on neat Alq₃ as EML was very poor. A closer investigation into the figure revealed that the current was very low, no more than 0.01 A. Thus devices exhibited a very low luminance (less than 500 cd/m²) and current efficiency (nearly 0.8 cd/A).

To increase the current through the devices, a hole transport material NPB was introduced to form a co-host EML [9]. It is easy to conclude from Fig. 5 that along with the increase of the portion of NPB in the co-host, all characteristics of the devices increased largely. This may be the result of the enhanced hole-injection from PVK into the EML by the introduction of NPB. From the energy level of this device shown in Fig. 1, we can see that as a result of the higher HOMO level of NPB than that of PVK, holes can easily be injected from the HOMO of PVK to that of NPB. Another reason for the increase of device performance after the introduction of NPB in the EML is the easy combination of excitons. Holes were injected into the EML to form NPB⁺, the cation of

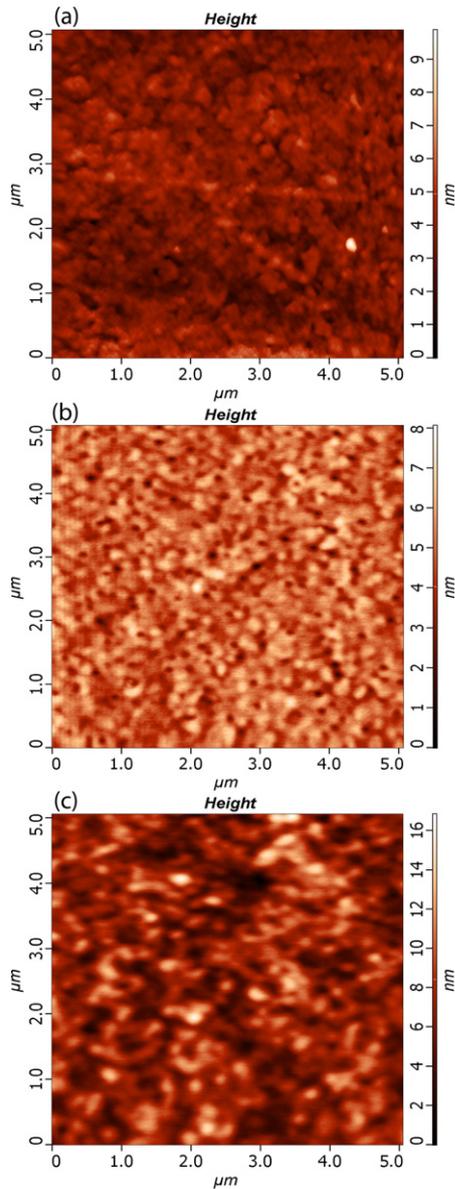


Fig. 4. (a) AFM images of PVK after three-component solvent system spin-coated on (b) AFM images of Alq₃ spin-coated from three-component solvent system solution (c) AFM of PVK/Alq₃ heterojunction layers by three-component solvent system.

NPB. The electrons were injected into ETL and transported into the EML to form Alq₃⁻ the anion of Alq₃. And then, NPB⁺ and Alq₃⁻ were recombined to form the Alq₃^{*}, which decays radiatively [26,27].

As shown in Fig. 5(a), the current multiplied from 0.009 A to 0.05 A when the ratio of NPB increased from 0 to 85% in the co-host, leading to a dramatic increase in luminance and current efficiency, from 500 cd/m² upward to 6200 cd/m², and 0.8 cd/A to 3.4 cd/A, respectively. We also compared the performance of these devices and those prepared through vapor-deposited method. From Fig. 6, we can see that the current efficiency is almost as high as the device by vapor-deposited method. That means that our system is suitable for the fabrication of multilayer OLEDs.

In fact, the dissolution of all polymers is subject to the same mechanism, and so are the small molecules, significantly, the conception of solvent/non-solvent system can be applied to other polymer/small molecule OLEDs by the correct choice of solvent and non-solvent.

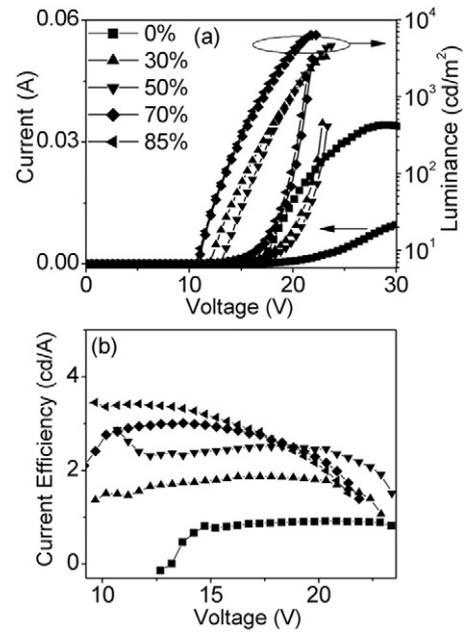


Fig. 5. (a) The current density–luminance–voltage and (b) efficiency–voltage characteristics of the devices at different NPB weight portions in the EML.

4. Conclusion

In conclusion, we utilized a solvent/non-solvent system to fabricate multilayer OLEDs based on polymer (PVK)/small molecule by solution process. It could efficiently prevent the second layer from intruding into the former one and thus enabled the multilayer OLEDs to be fabricated by solution process. In this study, we compared the film quality of PVK of two-component system and three-component system to conclude that, with the introduction of a third component DCE into the system, the thin films got smoother. Devices based on PVK/EML (NPB and Alq₃) prepared by this method exhibited the maximum luminance and current efficiency to be 6200 cd/m² and 3.4 cd/A, respectively, which could bear comparison with devices through the vacuum deposition.

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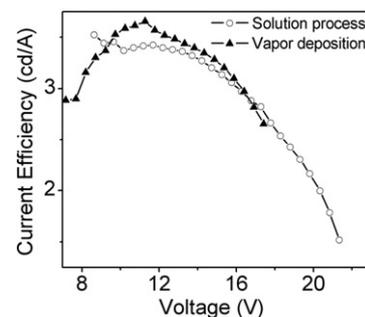


Fig. 6. Comparison of efficiency of device prepared by solution process and vapor-deposited method (the weight ratio of NPB to Alq₃ was fixed at 85:15).

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