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Coffee-Ring-Free Ultrasonic Spray Coating Single-Emission Layers for White Organic Light-Emitting Devices and Their Energy-Transfer Mechanism

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Supporting Information

ABSTRACT: Ultrasonic spray coating (USC) process is an alternative for low-cost solution-processed white organic lightemitting devices (OLEDs). However, complicated flow behaviors in the thick liquid layer, especially in multicomponent solution, result in the existence of ripples (coffee rings) in organic films. The ripples keep the USC process from being generally recognized as an efficient solution process for white OLEDs. Therefore, a slope method is proposed to avoid the emergence of ripples during the USC process. In the method, just like centrifugal force in a spin-coating process, gravity is used to remove redundant solution so that the remaining liquid layer can stay uniform under the control of substrate surface forces. Based on this, uniform organic films consisting of multiple components are obtained, and they are used as emitting layers to realize efficient white OLEDs. The white OLEDs based on the USC binary doping and ternary doping single-emission layer exhibit excellent electroluminescent performances. Furthermore, to clarify the energy transfer in the multicomponent emitting layers, their transient emission spectra are built based on the transient photoluminescent decay curves. And the detailed energy-transfer mechanism of the device is discussed.

KEYWORDS: ultrasonic spray, slope method, white emission, single emitting layer, OLEDs, energy transfer

INTRODUCTION

Due to high energy efficiency, eye-friendly emission, and flexibility, white organic light-emitting devices (WOLEDs) are emerging as a whole new invention of artificial lighting.^{1–13} During the past 25 years, WOLEDs have been obviously highly developed so that the WOLED lighting products start to come into the daily life of ordinary people. However, compared to conventional light sources, such as incandescent bulb, fluorescent tube, and light-emitting diode (LED) lamp, the prices of WOLED products are still much more expensive.

In terms of the manufacturing cost structure for OLED products, equipment depreciation and organic material costs are the two most important parts. These two parts of the cost stem from the vacuum thermal evaporation (VTE) process

which is usually used to fabricate OLEDs.^{14,15} To keep a highvacuum condition, the VTE process should be carried on by extremely complicated equipment that requires expensive routine maintenance. The material utilization of the VTE process is also not economical since over 75% of organic materials are wasted. Additionally, an emitting layer doped with multicomponent lumiphores or multiple emitting layers is needed to realize white emission.^{3,6,16,17} In VTE process, it is really difficult to realize the co-doping of three or more components, and compared with the former, the multilayer

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ACS Applied Energy Materials

approach is generally considered to complicate device fabrication and increase manufacturing cost.⁶

As a result, solution processes are proposed to reduce the cost of fabricating nanoscale organic thin films.¹⁸⁻²² The solution processes could allow straightforward deposition of a multicomponent layer and not need the condition of high vacuum. Ultrasonic spray coating (USC) process, which is a new deposition technology that has high material utilization, may be an alternative for solution-processed OLEDs, especially in large-scale industrial production. The application of USC process in polymer LEDs (PLEDs), organic photovoltaic cells (OPVCs), and organic thin-film transistors (OTFTs) has been demonstrated.²³⁻²⁸ However, the USC process is still not generally recognized as an efficient solution process for OLEDs. During the USC process, a uniform liquid layer is necessary to form continuous organic thin films. However, due to the limitation of surface tension and substrate surface energy, the liquid layer formed by the USC process is always much thicker than substrate surface forces could control. It is different from a spin-coating process in that there is no centrifugal force to remove excess solution in the USC process. Excess solution is hard to control by the substrate surface forces, such as van der Waals forces and electrostatic interactions.²⁹ Therefore, excess solution in the liquid layer could be obviously affected by its surface tension, and its complicated flow behavior, especially capillary flow, could not be ignored during the solvent evaporation. Finally, many ripples (coffee rings) occur in the formed organic film, leading to inhomogeneous film morphology.²⁴⁻²⁸ Since the thickness of conventional OLEDs is only about a hundred nanometers, the existence of ripples in films is very harmful for the application of these films in delicate OLEDs. To solve the problem, Girotto and co-workers have taken advantage of surface tension gradients to create Marangoni flows that enhance the coverage of the substrate and reduce the roughness of the film.²⁴ However, the requirements for solvents in two solvent systems are extremely strict.

Here, a slope method with general applicability is proposed to optimize the USC process. Through the slope method, gravity is used as the alternative of centrifugal force to remove excess solution and ensure the formation of an ultrathin liquid layer. Due to the restriction of substrate surface forces, the influence of flow behavior on the deposition of solute could become much weaker. As a result, uniform organic layers without any ripples are obtained by the USC process from the mixture solution consisting of multicomponent lumiphores.

Employing the uniform organic layers as an emitting layer, efficient white OLEDs with comparable electroluminescent performances to VTE OLEDs are realized. Furthermore, considering the complicated energy transfer between the multiple components, transient photoluminescent (PL) decay curves of the white emission layers are measured to characterize their energy-transfer mechanism. Besides, to clarify the mechanism more clearly, time-resolved emission spectra (TRES) of the white emission layer are built based on the transient PL decay curves.

RESULT AND DISCUSSION

The schemes of the USC fabrication process used in this work are shown in Figure 1.³⁰ In the process, organic solution is first atomized by the ultrasonic vibrational energy. Along with flowing nitrogen gas, the droplets reach the substrate under the ultrasonic nozzle and then recombine to form a continuous





Figure 1. Schemes of the USC fabrication process (a, conventional method; b, slope method).

liquid layer. To obtain an organic layer that meets the criterion of OLEDs, it is key to keep a uniform distribution of the liquid layer during the solvent evaporation.

However, the solution distribution could hardly remain unchanged in the conventional USC process as shown in Figure 1a. The formation of a liquid layer is affected by many factors, such as size and density of atomized droplets, wettability of solution, and surface energy of substrate. When a continuous liquid layer is formed, its thickness is always much larger than could be controlled by the substrate surface forces, such as van der Waals forces and electrostatic interactions.²⁹ Additionally, it is different from a spin-coating process in that there is no centrifugal force to remove excess solution in the USC process. By reason of the existence of excess solution, the influence of surface tensions and complicated flow behaviors should be considered.

As shown in Figure 2a, the droplet consists of the toluene solution of 4.4',4"-tris(carbazol-9-yl)-triphenylamine (TCTA) doped with binary lumiphores (components ratio is 9:1.5:0.1 TCTA:Firpic:Ir(MDQ)₂(acac), with bis(3,5-difluoro-2-(2pyridyl)phenyl(2-carboxypyridyl)iridium(III) (Firpic) and iridium(III) bis(2-methyldibenzo[f,h]quinoxaline)acetylacetonate $(Ir(MDQ)_2)$ that could spread out immediately and form a liquid layer after it drops on the PEDOT:PSScoated substrate (PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)). However, the liquid layer is not uniform since the solution at the edges is much thinner than that at the center. The nonuniformity of the liquid layer is obviously caused by the surface tensions as shown in Figure 2c. In the liquid layer with such distribution, the evaporation of toluene solvent can markedly influence the solution at the edge, while its influence on the solution at the center is much weaker. As the solvent evaporates, the differential concentration occurs between the edge and the center of the liquid layer, and the solution at the edge would finish the evaporation first. At the moment, the Marangoni flow and capillary flow (coffee-ring effect) should be considered.^{31–33} Because of the capillary effect, the liquid from the interior tends to replenish the liquid evaporating from the edge to keep the contact line.³¹ Moreover, the surface tension gradient induced by the differential concentration tends to redistribute solution back to the center of the liquid layer.³² Apparently, as shown in Figure 2c, there is a rivalry between Marangoni flow and



Figure 2. (a, b) Lateral view of droplet after it falls on PEDOT:PSS coated substrate placed on the flat and inclined plane and (c, d) schematic diagram of the film formation mechanism of the USC process based on conventional and slope methods.

capillary flow. However, these two flow behaviors are both complicated and uncontrolled,^{29,31-33} and it finally results in the instable deposition of solute at the edge of the liquid layer. Panels a and c of Figure 3 show the fluorescence microscope images of small molecular emitting layers fabricated by the



Figure 3. Photoluminescent (PL) fluorescence microscope images of small molecular emitting layers fabricated by the USC process based on (a, c) conventional method and (b, d) slope method. Panels a and b show the emitting layers consisting of red and blue lumiphores (RB-EML; component ratio is 9:1.5:0.1 TCTA:Firpic:Ir(MDQ)₂(acac)), and panels c and d show the ones consisting of red, green, and blue lumiphores (RGB-EML; component ratio is 9:1.5:0.15:0.225 TCTA:Firpic:Ir(mppy)₃:Ir(MDQ)₂(acac) with tris[2-(*p*-tolyl)-pyridine]iridium(III) (Ir(mppy)₃)); all the images are excited by a UV mercury lamp.

conventional USC process. The emitting layer consisting of red and blue lumiphores is marked as RB-EML, while the one consisting of red, green, and blue lumiphores is marked as RGB-EML. It can be seen in Figure 3a,c that many ripples exist in the organic films obtained by the conventional USC process.

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In order to make the USC process an efficient method for fabricating OLEDs, the problem of ripples should be solved. Here, through the slope method shown in Figure 1, gravity is used to remove the excess solution and ensure the formation of ultrathin liquid layer. It can be seen in Figure 2b that the solution flows downward along the slope in a very short time after the droplet falls on the substrate placed on the inclined plane. The flow of the solution should be attributed to the parallel component of gravity along the slope as shown in Figure 2d. Excess solution is removed under the effect of gravity, but an ultrathin liquid layer with a thickness corresponding to a few tens of molecules is still retained due to van der Waals forces and electrostatic interactions of the substrate.²⁹ The retained solution in the ultrathin liquid is closely absorbed by the surface forces on the substrate, and its flow behaviors are actually quite limited. Thus, the solute separated out from the solution is nearly the same at any location of the substrate. Finally, as seen in Figure 3b,d, highly uniform organic films RB-EML and RGB-EML without any ripples are obtained by the USC process with the slope method. Additionally, it is inevitable in the process of the slope method that some residual organic materials accumulate at the edge of the substrate. To eliminate the accumulation, degreasing cotton is put on the bottom of the substrate on the inclined plane to recycle the excess solution.

Furthermore, to gain information for the film morphology in microcosmic scale, atomic force microscope (AFM) images of small molecular emitting layers fabricated by the USC process with slope method are measured and shown in Figure 4. From the height images shown in Figure 4a,b, it can be found that



Figure 4. AFM images of small molecular emitting layers (a, c) RB-EML and (b, d) RGB-EML fabricated by the USC process with the slope method, and (e) their cross-section plots of topography images. Panels a and b are topography images, whereas panels c and d are phase images.

both RB-EML and RGB-EML are extremely smooth and their RMS roughnesses are 0.88 and 0.80 nm, respectively. The cross-section plots of their topography images are shown in Figure 4e. It is clear that the fluctuations of RB-EML and RGB-EML films in the Z direction are absolutely restricted within the limit of ± 2.5 nm. Additionally, only weak phase separation is observed from the phase images shown in Figure 4c,d. It can be concluded from the weak phase separation that there are only slight variations in the composition and topography of the surface. These above results indicate that the small molecular emitting layer fabricated by the USC process could completely satisfy the high requirement of OLEDs. The slope method establishes the foundation for the application of the USC process in the fabrication of nanoscale OLEDs.

Based on the USC small molecular emitting layer consisting of two and three lumiphores, efficient binary doping and ternary doping single-emission-layer white OLEDs are fabricated. The device structures of these white OLEDs and the chemical structures of the used small molecular materials are shown in Figure 5. TCTA with a high first-triplet energy level (T1) is used as the host material for phosphorescent lumiphores here.³⁴ 1,3,5-Tris[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) that is used as an electron transport layer has high T1 and deep HOMO so that it can efficiently confine triplet excitons and holes within the emitting layers.³⁵ The binary doping white OLEDs are realized by combining emission from Firpic and $Ir(MDQ)_2(acac)$, whereas the ternary doping white OLEDs are achieved by combining emission from Firpic, $Ir(mppy)_3$, and $Ir(MDQ)_2(acac)$.



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Figure 5. (a, b) Device structures of the white OLEDs based on USC emitting layers and (c) chemical structures of the used small molecule materials. The insets are pictures of these devices working at a current density of 10 mA/cm^2 .

First, the electroluminescent (EL) performances of the binary doping single-emission-layer white OLEDs are investigated. Figure 6 shows the current density-voltageluminance, current efficiency-luminance-power efficiency, and EL spectra characteristics of the binary doping white OLEDs. The two-color white OLEDs in which the emitting layer is fabricated by the USC process with the slope method are marked as USC-S. In addition, two other two-color white OLEDs are also fabricated for comparison. Although there are many sub-millimeter ripples in the emitting layer fabricated by the conventional USC process, the AFM image shown in Supporting Information Figure S1 indicates that the emitting layer still has a smooth nanoscale surface morphology. Thus, the device based on the emitting layer fabricated by the conventional USC process is used for comparison and marked as USC-C. Another is a device with an emitting layer fabricated by the vacuum thermal evaporation process, and the device structure is ITO/PEDOT:PSS/TCTA:Firpic:Ir(MDQ)₂(acac) (9:1.5:0.1, 40 nm)/TmPyPB (50 nm)/LiF(0.5 nm)/Mg:Ag (10:1, 120 nm). The vacuum thermal evaporation device is marked as VTE.

As seen in Figure 6, these three devices have a similar turnon voltage at about 3 V and achieve their maximum luminance at less than 10 V. The low turn-on and operating voltages give evidence of efficient carrier injection and transport in the USC emitting layers. Under the same operating voltage, the current density of VTE and USC-S is higher than the USC-C with rippled emitting layer. It should be attributed to the existence of ripples. The microscope images of USC-S and USC-C after being turned on at 5 mA/cm² are shown in Figure 6b,c, respectively. Uniform light emission could be observed over the whole devices area in the USC-S, whereas there are many ripples found in the USC-C. The peaks of ripples mean that these areas are much thicker than other areas in the emitting layer, resulting in a higher requirement for the operating voltage to realize carrier injection, transport, and recombina-

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Figure 6. (a) Current density-voltage-luminance, current efficiency-luminance-power efficiency, EQE-luminance, and EL spectra characteristics of the binary doping single-emission-layer white OLEDs, the microscope images of (b) USC-S and (c) USC-C after being turned on at 5 mA/cm², and (d) normalized EL spectra and CIE coordinates of USC-S under different bias voltages.

tion. As a result, only partial areas of USC-C work normally and the whole current of the device is limited to some extent by the large number of ripples. Due to the same reason, the luminance of USC-C is also much lower than that of USC-S. In general, the current density of these single-emitting-layer devices is limited. It should be attributed to there being a large number of $Ir(MDQ)_2(acac)$ molecules dispersing in the single emitting layer. Compared with the TCTA host materials, the deep HOMO and LUMO levels of $Ir(MDQ)_2(acac)$ make it serve as a strong carrier trap. Therefore, the wide existence of $Ir(MDQ)_2(acac)$ should strongly suppress the transport of carriers.³⁶ In the performance of maximum current, power, and external quantum efficiency (EQE), the difference between the USC devices is not significant. The maximum current, power efficiency, and EQE of the USC-S are 29.5 cd/A, 28.1 lm/W, and 14.1%, respectively. The USC-C performs nearly as well as the USC-S, and its maximum current, power efficiency, and EQE are 27.8 cd/A,24.9 lm/W, and 13.1%, respectively. It should be attributed to the existence of partial areas that could function in a normal way. At low bias voltage, these partial areas could still be turned on and produce electroluminescence normally, whereas thicker areas are nearly out of function and do not make any contribution to current or luminous emission.



Figure 7. (a) Current density-voltage-luminance, current efficiency-luminance-power efficiency, EQE-luminance, and EL spectra characteristics (at 4 V) of the ternary doping single-emission-layer white OLEDs with the optimized USC emitting layer, and the energy diagram and exciton dynamics for (b) binary doping and (c) ternary doping single-emission-layer white OLEDs with the USC emitting layer.

Besides, the power efficiency is not relevant to active device areas, so the maximum power efficiency of the USC-C device is not much lower than that of the USC-S device. However, the case is different at high bias voltage since the thicker areas could also be turned on and begin to make contribution to the whole current and luminous emission. At the time, as seen in the Figure 3, the power efficiency of the USC-C device could be influenced by the thicker areas and become much lower than that of the USC-S device. Additionally, compared to the USC devices, the efficiency of the vacuum thermal evaporation device VTE is a little higher. The maximum current, power efficiency, and EQE of the VTE-D are 29.9 cd/A,29.3 lm/W, and 13.8%, respectively. The difference in efficiency between the vacuum thermal evaporation device and the USC device may be caused by the introduction of impurity in the USC process carried on in the atmosphere.³⁷ Therefore, an ultraclean golvebox with an ultralow concentration of oxygen and water is necessary for the fabrication of USC organic films.

The EL spectra of these binary doping single-emission-layer white devices at 4 V are also shown in Figure 6a. It could be

clearly observed that all the EL spectra of these white devices are composed of blue and red emission corresponding to Firpic and Ir(MDQ)₂(acac), respectively. EL spectra of the USC-S are nearly identical to those of the USC-C except for a slight change at the wavelength of about 500 nm. It indicates that the existence of ripples only has a little influence on the EL spectra. Additionally, the Commission Internationale de L'Eclairage (CIE) coordinates of the USC-S and USC-C at 4 V are (0.355, 0.389) and (0.353, 0.392), respectively. Figure 3d shows the normalized EL spectra and CIE coordinates of USC-S under different bias voltages. When the bias voltage is lower than 6 V, the relative intensity of the blue emission increases with bias voltage compared with the red emission. It should be attributed to the direct charge trapping effect³⁶ of Ir-(MDQ)₂(acac) playing an important role on red emission under low bias voltage. As the voltage increases, the carriers trap in $Ir(MDQ)_2(acac)$ should be saturated and more carriers are transferred to TCTA molecules. The emissions under high bias voltage begin to mainly depend on energy transfer from



Figure 8. (a) Photoluminescent (PL) spectra and absorption spectra of the materials in the USC multicomponent emitting layer; (b-d) transient PL decay curves of the USC emitting layers with various lumiphores.

excitons formed in the TCTA molecules. Therefore, the EL spectra could be stable under high bias voltage.

According to all of the above results, it could be found that the elimination of ripples could not only realize uniform light emission but also obviously improve the current density and luminance of devices. Meanwhile, the efficiency and EL spectra of devices can be kept unchanged after getting rid of ripples. Besides, to some extent, the EL performances of the USC devices could be comparable to the vacuum thermal evaporation devices.

Subsequently, the ternary doping single-emission-layer white OLEDs employing the optimized USC emitting layers are also realized and their EL performances are studied. Figure 7 shows the current density-voltage-luminance, current efficiencyluminance-power efficiency, and EL spectra characteristics of the ternary doping white OLEDs. The ternary doping white OLEDs are turned on at 3 V and attain their maximum luminance at 9.5 V. The maximum current and power efficiency of the ternary doping white OLEDs is 26.9 cd/A and 25.1 lm/W, respectively. Blue, green, and red emissions could be found in the EL spectra of the white OLEDs, and these emissions are produced by Firpic, Ir(mppy)₃, and $Ir(MDQ)_2(acac)$, respectively. The EL performances of these white OLEDs are collected in Table S1. The performances of the binary and ternary doping OLEDs provide evidence for the application of the USC process in fabricating nanoscale multicomponent organic films.

Finally, the energy-transfer mechanisms in the multicomponent emitting layers fabricated by the USC process for white OLEDs are summarized in Figure 7b,c. PEDOT:PSS is an efficient hole injection and transport layer so that holes could be easily injected into the emitting layer from ITO anode. Due to the trapping effect, partial injected holes are trapped into the lumiphores with shallow energy level. But most injected holes transport along the TCTA molecules and accumulate at the interface between TCTA and TmPyPhB. After the electrons are injected into the emitting layer, most of them would recombine with the accumulated holes and form excitons at the interface between TCTA and TmPyPhB. As a result, the energy transfer of the excitons formed at the interface between TCTA and TmPyPhB plays an important role in the light emission of the white OLEDs.

To verify the energy-transfer mechanisms, the photoluminescent (PL) spectra and absorption spectra of the materials in the multicomponent emitting layer are measured and shown in Figure 8. From the absorption spectra shown in Figure 8a, it can be found that the metal-to-ligand chargetransfer bands from singlet (¹MLCT) and triplet (³MLCT) in Firpic is resolved at 380 and 450 nm, respectively, whereas the ¹MLCT and ³MLCT of Ir(mppy)₃ are observed at 390 and 480 nm, respectively.^{38,39} Considering their large overlap with both the PL spectra and the reported phosphorescence spectra of TCTA,⁴⁰ an efficient energy-transfer process from TCTA to FIrpic or $Ir(mppy)_3$ is anticipated. However, the case is different for the energy-transfer process from TCTA to $Ir(MDQ)_2(acac)$. The phosphorescence spectra of TCTA (between 440 and 500 nm) do not overlap very well with the $^{3}MLCT$ of $Ir(MDQ)_{2}(acac)$. Thus, the triplet energy transfer from TCTA to Ir(MDQ)₂(acac) may not be sufficient.

Additionally, the transient PL decays of the emitting layers with various lumiphores (all the emitting layers here are fabricated by the USC process with the slope method) are measured by time-correlated single-photon-counting technique to clarify the energy transfer between the multiple lumiphores clearly. As shown in Figure 8b, there is no change found in the decay of blue emission from the Firpic molecules after the introduction of $Ir(mppy)_3$. However, the decay of blue emission in the TCTA film doped with Firpic and $Ir(MDQ)_2(acac)$ becomes much faster than that in the Firpic-only-doped TCTA film. These results indicate that the existence of energy transfer from Firpic to $Ir(mppy)_3$ is a remote possibility, whereas the energy transfer from Firpic to Ir(MDQ)₂(acac) obviously occurs in the co-doped system. Additionally, it can be seen in Figure 8c that the introduction of additional Ir(MDQ)₂(acac) also accelerates the decay of green emission from the $Ir(mppy)_3$ molecules. Thus, excitons could be also transferred from the Ir(mppy)₃ to Ir- $(MDQ)_2(acac)$ in the multicomponent emitting layer. The



Figure 9. Time-resolved emission spectra of the (a, b) binary doping and (c, d) ternary doping single-emission layers fabricated by the USC process with the slope method. Panels a and c are line graphs, whereas panels b and d are contour patterns.

decay of red emission from $Ir(MDQ)_2(acac)$ in the binary doping and ternary doping single-emission layers is also studied as shown in Figure 8d. The same results in the two types of emitting layers confirm the conclusion that there is no energy transfer between Firpic and $Ir(mppy)_3$ since the decay can be prolonged by the indirect energy transfer.

Furthermore, time-resolved emission spectra (TRES) of the USC multicomponent emitting layers are obtained based on their transient PL decay curves measured at different wavelengths covering the visible range. TRES are an efficient characteristic for understanding the exciton dynamics existing in the emitting layer, especially the ones with multiple components. TRES of binary doping single-emission layers are shown in Figure 9a,b. At the initial stage, only the purplish blue emission from TCTA occurs, noting that excitons are formed in the TCTA molecules. Subsequently, emission from TCTA begins to disappear gradually and emission of Firpic comes in slightly. It is clear that the emergence of blue emission is induced by the transfer of excitons from TCTA to the Firpic. As time goes on, red emission is observed at some point and its intensity is getting stronger until the steady-state emission spectra are obtained. Apparently, the red emission arises from the $Ir(MDQ)_2(acac)$ molecules. Since the emergence of red emission is significantly delayed compared to blue emission, excitons of Ir(MDQ)₂(acac) should be transferred from the Firpic rather than directly from the TCTA. Therefore, TRES verify that there is no direct energy transfer from TCTA to $Ir(MDQ)_2(acac)$ in the binary doping single-emission layers.

Similarly, TRES of ternary doping single-emission layer are obtained and shown in Figure 9c,d. The case is the same in that only the purplish blue emission from TCTA is observed at first. However, after the purplish blue emission disappears, bluish green emission in a much broader range between 450 and 600 nm emerges. Obviously, the broader bluish green emission should be caused by the co-occurrence of emission

from Firpic and $Ir(mppy)_3$. The results accord well with the conclusion that excitons for the emission of $Ir(mppy)_3$ can be directly transferred from the TCTA without the aid of Firpic. As time goes on, red emission from $Ir(MDQ)_2(acac)$ appears and develops into the predominant part of the whole white emission soon afterward. This phenomenon indicates that most excitons transferred from TCTA to both Firpic and $Ir(mppy)_3$ are transferred into $Ir(MDQ)_2(acac)$ finally. It can be found that the information provided by TRES of the multicomponent emitting layers can visually characterize the proposed excitons dynamic shown in Figure 7b,c.

CONCLUSION

In summary, a slope method is proposed to utilize the gravity of solution in the USC process. Under the action of gravity, unnecessary solution is removed and an ultrathin liquid layer controlled by substrate surface forces is obtained. After the solvent evaporates, uniform organic films without any ripples are separated out from the solution consisting of multiple components. These uniform organic films also have extremely smooth surfaces in microcosmic scale since their surface RMS roughness is lower than 1 nm. Employing these uniform USC organic films as emitting layers, binary doping and ternary doping single-emission-layer white OLEDs are fabricated. These white devices have low turn-on and operating voltages. The maximum current and power efficiency of the binary doping and ternary doping single-emission-layer white OLEDs can be attained at 29.5 cd/A, 28.1 lm/W and 26.9 cd/A, 25.1 lm/W, respectively. Based on the information from their TRES, it can be found that excitons formed in the TCTA can directly transfer to Firpic and Ir(mppy)₃ but transfer to $Ir(MDQ)_2(acac)$ indirectly via Firpic or $Ir(mppy)_3$. This work would be beneficial to the development of low-cost white OLEDs based on the USC process.

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EXPERIMENTAL SECTION

Device Fabrication. Small molecular organic materials, such as 4,4',4"-tris(carbazol-9-yl)-triphenylamine (TCTA), 1,3,5-tris[(3-pyridyl)-phen-3-yl]benzene (TmPyPB), tris[2-(p-tolyl)pyridine]iridium-(III) $[Ir(mppy)_3]$, iridium(III) bis(2-methyldibenzo[f,h]quinoxaline)acetylacetonate [Ir(MDQ)₂(acac)], and bis(3,5-difluoro-2-(2pyridyl)phenyl(2-carboxypyridyl)iridium(III) (Firpic), are purchased from Luminescence Technology Corp. Polymer material poly(3,4ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is obtained from Xi'an p-OLED. All of the devices are fabricated on glass substrates that are commercially precoated with an indium-tin oxide (ITO) anode. The substrates are washed carefully by Decon 90 before they are cleaned three times in ultrasonic baths of deionized water for 5 min each and are then baked at 120 °C in an oven. Before film deposition, the cleaned ITO substrates are treated for 3 min in a plasma cleaner chamber. The PEDOT:PSS films are fabricated by spin-coating process at 4000 rpm for 1 min from PEDOT:PSS aqueous solution (Baytron CH-8000), and then the PEDOT:PSS films are annealed at 120 °C for 15 min. The small molecular white emission layers are directly fabricated by USC process from the toluene solution of TCTA doped with three lumiphores [Firpic, Ir(mppy)₃, and Ir(MDQ)₂(acac)] or two lumiphores [Firpic and $Ir(MDQ)_2(acac)$]. The mass fraction of the solution is 1–10 mg/mL, the mass ratio of TCTA, Firpic, Ir(mppy)₃, and Ir(MDQ)₂(acac) in three lumiphores solution is 9:1.5:0.15:0.225, and the mass ratio of TCTA, Firpic, and Ir(MDQ)₂(acac) in two lumiphores solution is 9:1.5:0.1. The USC process is carried on by the UC320 system (Siansonic Technology Co.) employing a D series ultrasonic nozzle. The USC process is carried on in confined space with a saturated vapor of toluene. The ultrasonic nozzle is put on top of the substrate, and its height is about 6 cm. The substrate is placed on the flat plane or inclined plane without heating during the film formation process, respectively. The solution is injected into the ultrasonic spray nozzle at the speed of 0.2 mL/min. The scanning speed and width are 100 mm/s and 1 mm, respectively. The binary or ternary solution concentration and the injection volume for the substrate on flat plane are 1.06 or 1.09 mg/mL and 100 μ L, respectively, whereas the binary or ternary solution concentration and the injection volume for the substrate on inclined plane are 10.6 or 10.9 mg/mL and 50 μ L, respectively. Besides, the degreasing cotton is put on the bottom of the substrate on an inclined plane to recycle the excess solution. After the organic films are obtained, the films are annealed at 80 °C for 15 min to remove residual solvent. The electron transport layer (TmPyPB, 50 nm) and cathode (Mg:Ag, 10:1, 120 nm) are evaporated by VTE process under high vacuum ($\sim 5 \times 10^{-4}$ Pa) at a rate of 1-2 Å s⁻¹ monitored in situ with a quartz oscillator. A metal pattern plate is used to define the cathode and makes four 10 mm² devices on each substrate.

Film and Device Characterization. The static lateral images after droplets fall on the substrate are measured using a contact angle goniometer (JC2000D contact Angle Meter, Powereach Co. Shanghai, China). The microcosmic and macroscopic morphologies of the USC organic layers are characterized by using atomic force microscopy (Dimension Icon, Bruker Co.) and Mshot M53 inverted fluorescence microscope with a mercury lamp UV excitation source and MCX2 CCD camera, respectively. The microscope images of OLEDs are driven by Keithley 2400 and measured by Mshot M53 inverted fluorescence microscope. The thickness of ultrasonic spray coating films is adjusted by an ellipsometer (J. A. Woollam Co. Inc.). Luminance-current-voltage characteristics and spectra of unpackaged devices are measured simultaneously using a Goniophotometric Measurement System based on a spectrometer (GP-500, Otsuka Electronics Co., Osaka, Japan) in air at room temperature. The transient photoluminescence decay curves of the white emission layer are obtained by the IHR320 spectrometer (HORIBA, USA) with the excitation light source at 290 nm.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.7b00011.

AFM images for emitting layers fabricated by the conventional USC process; EL performances of these white OLEDs (PDF)

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Author Contributions

S.L. designed and conducted most of the experiments, analyzed the data, and prepared the manuscript. X.Z. helped with most of the experiments. M.Y. implemented the measurements of atom force microscope imaging. H.F. contributed to static lateral viewing measurement. J.Z. carried out the transient photoluminescent decay experiments. L.Z. gave some significant comments on the experiments and data analysis. W.X. initiated the study, designed all the experiments, analyzed the data, and prepared the manuscript. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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112