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Two-dimensional-growth small molecular hole-transporting layer by ultrasonic spray coating for organic light-emitting devices



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ABSTRACT

Two-dimensional-growth small molecular organic thin film with high quality is fabricated by ultrasonic spray coating technology (USC) from the toluene solution of 4,4',4"-tris (carbazol-9-yl) triphenylamine (TCTA). In comparison to the vacuum thermal evaporation (VTE) TCTA film, the USC-TCTA film obtained from liquid-phase solution possesses more uniform surface topography. The differences between the USC-TCTA and the VTE-TCTA in optical property, electrical property and formation mechanism are also studied in detail. Besides, to evaluate the hole transport and electron blocking ability of USC-TCTA film, the organic light-emitting devices (OLEDs) employing USC-TCTA film as hole transport layer are fabricated successfully. Additionally, the green OLEDs based on USC-TCTA film perform as well as the ones with VTE-TCTA film in current density, luminance, efficiency and color stability, and show even better tolerance to high bias voltage.

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1. Introduction

Organic light-emitting devices (OLEDs) have been developed remarkably in the past thirty years [1-7]. The smartphone, television, tablet computer, VR containing OLED display panel and lamp employing OLED lighting panel mean the beginning of the practical process of OLED. However, high manufacture cost of the common vacuum thermal evaporation (VTE) OLEDs is still hindering the application of OLEDs. The high manufacture cost should be attributed to the complicated equipment and low materials utilization [8,9]. Besides, the growth mechanism of thin film in vapor phase growth techniques is strongly dependent on the substrate surface energy and the interaction between atoms or molecules. Thus, the growth of the thin film may be one of three modes as follows: island growth, Frank-vander Merwe growth and Stranski-Krastanov growth [10–15]. Additionally, the defects and impurities existing in substrate, the material impurities and the impact of the residual

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gas could also obviously affect the growth of thin film [16]. Thus, these properties of VTE process would be harmful to quality control in large-scale industrial production.

To reduce the manufacture costs, solution process, especially spin coating process, is proposed to substitute the VTE process for the OLEDs' fabrication. Although spin coating process has been proved to be suitable to fabricate laboratorial devices, it still has some difficulties for large-scale industrial production, efficient material utilization and low-viscidity organic solution [17,18]. Especially, due to the limitation on solubility, molecular chains and weight, the viscidity of small molecular organic materials is usually too low to employ the spin coating process, obstructing the application of spin-coating process in manufacturing small molecular OLEDs [19–21].

Hence, the ultrasonic spray coating (USC) deposition technique has caught researchers' attention in fabricating photoelectric devices recently. This process exhibits a high material utilization ratio over 90%, practicability for industrial production line and compatibility to low-viscidity organic solution [22–24]. Thus, it may offer the possibility to avoid the problems indicated above. In the recent years, the USC deposition technique has been proved as an efficient method to realize excellent organic solar cells, organic thin-film transistors and polymer light-emitting diodes [25–31]. However,



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till now, almost all the reported USC thin films used for photoelectric devices rely on polymer materials.

Therefore, evidences are still needed to prove the feasibility of USC deposition technique in realizing thin films based on small molecular organic materials. 4,4',4"-Tris(carbazol-9-yl) triphenylamine (TCTA) is a common hole transport material in OLED, and it performs well in hole carriers transport, electron carriers and excitons blocking, and film stability since it possesses high triplet energy, hole transport ability and glass transition temperature [32–36]. Besides, uniform TCTA films could be obtained by either solution process or vacuum deposition [33,36]. Thus, the TCTA is adopted to fabricate organic thin film in the USC process here. A high quality TCTA film is successfully obtained, and the differences between the USC film and the VTE film in optical property, electrical property and formation mechanism are studied in detail. Besides, the USC-TCTA film is introduced into the OLEDs to verify its effectiveness. The green OLEDs employing USC-TCTA film as hole transporting layer are successfully fabricated and their electroluminescent performances are studied in detail.

2. Experimental

2.1. Device fabrication

The small molecular organic materials: 4,7-Diphenyl-1,10phenanthroline (Bphen), 4,4'-Bis(carbazol-9-yl)biphenyl (CBP) and TCTA used in our experiments are purchased from Luminescence Technology Corporation, while the green phosphor tris(2phenylpyridine)iridium(III) $[Ir(ppy)_3]$ and polv(3.4ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, PH8000) are obtained from Xi'an *p*-OLED. Before film deposition, the ITO glass substrates are subjected to a routine cleaning process with rinsing in Decon 90, deionized water, drying in an oven, and finally treating in a plasma cleaner chamber. The PEDOT:PSS films are fabricated by spin coating from aqueous solution, and then the PEDOT:PSS films are all annealed at 120 °C for 15min.

The TCTA toluene solution (1 mg/mL) is used to form the small molecular hole transporting layer on PEDOT:PSS film through the USC process. The USC process is carried on in ultrasonic spray coating system (UC320, Siansonic Technology Co. Beijing, China) employing D series ultrasonic nozzle. The ultrasonic nozzle is put on the top of heating plate, and the distance is fixed to 10 cm to avoid the influence of carrier gas on the liquid layer formed on the substrate. The TCTA toluene fluid is injected into the ultrasonic spray nozzle with the speed of 3 ml/min, and under the effect of 1 MHz ultrasonic vibrational energy, the TCTA toluene fluid is atomized to micrometer-scale drops. To obtain the targeted TCTA film, the injection volume is set to 120 µL. And the temperature of the heating plate that the micrometer-scale drops fall on is 40 °C, and then the targeted film is annealed at 100 °C for 15 min. After that, the emitting layers, carrier transfer layers and cathode 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. Finally, there are four 10 mm² devices fabricated on each substrate, and the active area of the devices is decided by overlap between anode and cathode.

2.2. Device characterization

The static lateral images are measured using a contact angle goniometer (JC2000D, Powereach Co., Shanghai, China), while the surface morphologies of the films are characterized by using atomic force microscopy (AFM, Dimension Icon, Bruker Co., Germany) in contact mode. The fluorescence microscopy images are obtained by the inverted fluorescence microscope (Mshot M53, Micro-shot Technology Co. Ltd., Guangzhou, China). The impedance characteristics of the devices are carried on at room temperature employing using precision LCR meter (TH2829C, Tonghui, Changzhou, China) at the frequency of 1 KHz with the oscillation amplitude of the ac voltage keep at 0.1 V. Luminance-currentvoltage characteristics and spectra of unpackaged devices are measured simultaneously using Goniophotometric Measurement System based on spectrometer (GP-500, Otsuka Electronics Co., Osaka, Japan) in air at room temperature.

3. Result and discussion

3.1. Fabrication of USC-TCTA film

In the USC process, the liquid organic solution is first transformed into dense micrometer-scale droplets by ultrasonic atomizer. Following the carrier nitrogen gas, the atomized droplets would reach to the ITO substrate and merge with each other to reform a continuous liquid layer with only several micrometers thickness [37]. Under the influence of heating plate, the solvent of the liquid layer would evaporate and the residual solute is then cured into solid thin film. It should be emphasized that the uniform distribution of liquid layer during solvent evaporation stage is the guarantee for obtaining the high-quality targeted film through the USC process. Thus, the wettability of TCTA toluene solution on PEDOT: PSS film is firstly studied as indicated in Fig. 1 (a) which are the lateral pictures of TCTA toluene solution droplet after dropping on the PEDOT:PSS film. It can be seen that the droplet immediately spread out to form a liquid thin film at the time it falls on the substrate, and the distribution of the liquid layer could keep relatively homogeneous wherever it covers. It could mean that the surface tension existing in the wetting layer isn't strong enough to induce it to shrink during the solvent evaporating stage.

3.2. Surface topography of TCTA films

Therefore, based on the TCTA toluene solution, the uniform TCTA thin film with high quality is successfully fabricated. It can be seen from the AFM surface topographical images (Fig. 2) that the 30 nm USC-TCTA (sTCTA) film exhibits distinctly different surface topography with the 30 nm VTE-TCTA (eTCTA) one. The sTCTA film even possesses more uniform surface and lower roughness. Additionally, the Wenzel equation indicates that the contact angle decreases as the surface roughness increases when the contact angle is lower 90° [38]. Therefore, as seen in Fig. 2 (g) and (h), the larger contact angle of water on the sTCTA film also confirms its more flat surface. The difference in surface topography between the films fabricated by different processes should be attributed to the different film formation mechanisms.

In the VTE process, the growth of organic thin film would rely strongly on the interaction strength between organic molecule and substrate surface due to the atom-by-atom or molecule-by-molecule depositing style of these kinds vapor phase deposition techniques [13–15]. Under the condition that the organic molecule can more strongly bound to each other than to substrate, it prefers to form three-dimensional islands on the substrate initially. And then, as the islands grow larger, these islands would connect with each other and finally form a continuous film whose surface topography is just like that shown in Fig. 2 (a). To verify the Volmer-Webber growth of eTCTA fabricated by VTE process, a very thin eTCTA film with only 10 nm is also fabricated to simulate the initial stage of the growth. The AFM surface topographical and phase-contrast image of the eTCTA with 10 nm is shown in Fig. 2 (e) and (f), respectively. It can be clearly seen in the phase-contrast



Fig. 1. (a) The lateral pictures of TCTA toluene solution droplet after dropping on the PEDOT:PSS film and (b) the schematic diagram of film formation during solvent evaporation stage.

image that many isolated islands with different sizes are evenly distributed on the substrate, while such information is not found in the corresponding topographical image. Thus, the isolated islands existing in the phase-contrast image should arise from compositional variations rather than the topographical variations of the surface [39]. The results could verify the existence of TCTA islands and the Volmer-Webber growth of VTE-TCTA.

With regard to the USC process, the TCTA film formation mechanism belongs to liquid-phase deposition technique. The film formation during the solvent evaporation stage of the USC process is distinctly different to that from vapor phase in the VTE process. It should belong to the two-dimensional-growth mode and its filmformation schematic diagram is shown in Fig. 1 (b). Due to the rapid random thermal motion of the molecules [40], the TCTA small organic molecule could be evenly dispersed in the toluene solution, even during the solvent evaporating stage. Hence, when the liquid layer of TCTA toluene solution could keep the uniform condition, the existing TCTA solute would be same in any location on the substrate. Additionally, when the toluene is evaporating gradually, the thermal motion ranges of TCTA molecules come to be restricted to a much smaller space. And then, the TCTA small molecular chains would have adequate opportunity to entangle with each other [36]. As the weight of the intertwining small molecular chains reach to a certain extent, these intertwining chains would deposit layer-bylayer on the substrate to form the film whose surface topography is just as shown in Fig. 2 (b).

Beyond that, the TCTA films fabricated by different process also have some influences on the growth of emitting layer (EML) deposited on them. As indicated in Fig. 2 (c) and (d), the EML consisting of CBP doped with 10 wt% Ir(ppy)₃ on sTCTA is also more uniform than that on VTE-TCTA. The difference of EMLs in surface topographical images should be attributed to different surface energy distribution on the two TCTA films. The Volmer-Webber growth of VTE-TCTA could result in the variation of surface energy at different region while the sTCTA film with high uniformity could ensure it identical everywhere. Thus, the growth of EML on VTE-TCTA on sTCTA would prefer to be islands growth and twodimensional-growth, respectively, leading to the difference in their surface topography.

To evaluate the film uniformity in larger scale, the fluorescence microscope pictures of sTCTA and eTCTA films doped with 5 wt% Tris[2-(p-tolyl)pyridine]iridium(III) [Ir(mppy)₃] is measured and the pictures are shown in Fig. 2 (i) and (j). From the fluorescence pictures, it could be seen that both the sTCTA and eTCTA films could perform well in hundred micrometer scale. However, compared to the eTCTA film, there are some ripples in the sTCTA film. The ripples existing in the sTCTA film should be caused by the coffee stain effects after the fully covering wetting layer begin to fade away to form the solid film. When the liquid layer is thick, the excellent wettability characteristic of TCTA toluene solution on PEDOT:PSS could ensure that the liquid layer fully covers the substrate. Besides, different evaporation rate may produce some depression zone and concentration difference. Since the TCTA molecule has no amphiphilic groups and hydrogen bond, the TCTA solute could not be the surfactant. Thus, the increase of concentration in the depressed zone would lead to the increase of surface tension. Due to the Marangoni effect induced by the surface tension difference [41], the liquid in other zone would flow into the depressed zone so that the liquid layer could be kept uniform. Nevertheless, when the liquid layer is too thin to cover the whole substrate, there is no solution with higher surface tension in the depression zone to draw the solution nearby for smoothing the liquid layer. At the moment, the fully covering wetting layer begin to fade away to form the solid film. And then, the influence of coffee stain effect begins to emerge since the liquid from the interior would tend to replenish the disappearing edge due to capillary flow [42]. Hence, the inflow of extra solution would result in the increase of TCTA solute at edge and produce the ripples in the sTCTA film. However, because of the excellent wettability of TCTA toluene solution and low being point of toluene, the disappearing liquid layer is extremely thin and its



Fig. 2. (a) (b) (c) (d) (e) the AFM surface topographical images of eTCTA (30 nm), sTCTA (30 nm), EML (30 nm) on eTCTA, EML (30 nm) on sTCTA and eTCTA(10 nm), (f) the AFM surface phase-contrast images of eTCTA (10 nm) (all the size of the AFM images is $5 \times 5 \mu$ m), (g) (h) the contact angle pictures of water on sTCTA and eTCTA and (i) (j) the fluorescence microscope picture of sTCTA and eTCTA films doped with 5 wt% Ir(mppy)₃.

evaporation rate is very fast. Thus, the capillary flow is under restrictions to some extent so that the fluctuations of ripples are slight.

3.3. Optical property of TCTA films

Although there are obvious differences in surface topography between the two TCTA films, the optical properties of sTCTA are nearly as same as those of eTCTA. As seen in Fig. 3 (a), in addition to a little gap in the range between 525 and 625 nm, the transmittance and absorbance of sTCTA coincide well with those of eTCTA in the visible wavelength region. It indicates that the USC process would not have a distinct effect on the optical properties in the visible wavelength region. Additionally, the little gap in the range between 525 and 625 nm should be attributed to the different film density, since the solution and vacuum process could make a difference in film density [43,44]. Additionally, the different film density could also be reflected in the surface topography shown in Fig. 2. To observe the quenching effect of the sTCTA film on emission from emitting layer, the emitting layers consisting of CBP doped with 10 wt% Ir(ppy)₃ are deposited on the TCTA films and their time-resolved photoluminescence spectra are measured. It could be found that emission from emitting layer on sTCTA possesses same decay tendency to the one from emitting layer on eTCTA.

3.4. Hole transport ability of TCTA films

Furthermore, the hole transporting property of the sTCTA is also



Fig. 3. (a) The transmittance and absorbance characteristics of sTCTA (30 nm) and eTCTA (30 nm) on PEDOT:PSS, (b) the time-resolved photoluminescence spectra of the emitting layer deposited on sTCTA and eTCTA, (c)the Cole-Cole plots and (d) the imaginary part of impedance of the hole-only device based on TCTA films at frequency from 1 KHz to 1 MHz under 10 V bias voltage.

studied. To evaluate the hole transport ability of sTCTA and eTCTA, the performances of alternating small-signal with different frequencies in single-carrier devices based on TCTA films are discussed. The introduction of small-amplitude alternating voltage will induce the redistribution of a small minority of carriers. The carrier redistribution could produce a small alternating current lagging behind the voltage so that the impedance (Z) characteristics of the single-carrier devices could be observed [45-48]. Based on that, the Cole-Cole plots and the imaginary part of impedance [Im(Z)] of the hole-only device based on TCTA films at frequency from 1 KHz to 1 MHz under 10 V bias voltage is obtained and shown in Fig. 3 (b) and (c). The semicircles shown by the Cole-Cole plots mean that the TCTA single-carrier devices could be simulated by the parallel connection of a resistance (R_p) and a capacitance (C_p) [45-47]. Additionally, since the plots do not pass through the origin, an extra resistance (Rs) should be connected in series to the R_pC_p parallel circuit above so that the equivalent circuit of the single-carrier devices should be the one shown in Fig. 4 (b). Thus, the impedance of the single-carrier devices could be expressed as

$$Z = R + iX = \left[R_{\rm s} + \frac{R_p}{1 + (\omega R_P C_P)^2} \right] - i \left[\frac{\omega R_P^2 C_P}{1 + (\omega R_P C_P)^2} \right]$$
[46]. Besides, the

equivalent circuit could also be validated by the physical mechanism of carriers in the single-carrier devices. The energy level diagram of the single-carrier devices is also shown in Fig. 4, and the values of the corresponding energy levels are derived from references [4,49,50]. It can be seen that there are energy barriers for hole and electron carriers injecting from anode and cathode to TCTA so that hole and electron carriers could be accumulated at the interface of anode/TCTA and cathode/TCTA, respectively. The accumulated carriers could make the devices possess the capacitance characteristics. Due to the high energy level difference between the work function of electrode and the LUMO of TCTA, the electron carriers are hard to enter into the TCTA films. However, hole carriers could pass thorough the TCTA films to make a contribution to current when a certain bias voltage is applied on the single-carrier devices. Thus, the existence of resistance characteristics is also explicit.

However, the case would be different when the frequency of small-signal is too high to such an extent that the hole carriers has no enough time to traverse the TCTA film. The high frequency leads to that the hole carriers can't pass through the film to produce current signal in one small-signal period. As a consequence, only the capacitance characteristic could affect the obtained alternate current signal and the resistance characteristic of the single-carrier devices is regarded as infinity. Thus, the equation expression of the impedance could become to $Z = R + iX = R_s - i \frac{1}{\omega C_P}$. It could be also speculated that the equivalent circuit of the single-carrier devices becomes to the series connection of R_s and C_p as shown in Fig. 4 (d). Furthermore, after the angular frequency ω is changed to frequency f, the relation between Im(Z) and the frequency f is obtained from $\ln(-X) = \ln \frac{1}{\omega C_P} = -\ln f - \ln 2 \pi C_P$. It can be clearly seen that there is a linear relation between the logarithm of negative Im(Z) and the logarithm of frequency *f*.

Considering above, the Im(Z) detected by the alternative smallsignal would be obviously different in low frequency and high frequency region. Besides, the transition frequency should be related to the reciprocal of the transit time that hole carriers need to traverse the TCTA film. Thus, the hole transport ability of sTCTA and eTCTA could be evaluated based on the transition frequency. As seen in Fig. 3 (c), both for sTCTA and eTCTA, the absolute value of Im(Z) increases with frequency in the low frequency region. It should be attributed to that the effect of the capacitance



Fig. 4. (a) (c)the hole carriers transport mechanism in energy level diagram detected by low and high frequency small-signal. (b) (d) the equivalent circuits of single-carrier devices in low and high frequency.

characteristic on the small-signal current is turning to be more and more important than that of the resistance characteristic. Additionally, it could also be seen that the Im(Z)-*f* curves become to a straight line in the double-exponential coordinate system when the frequency *f* is very high. It indicates that only the capacitance characteristic of the devices is presented just like what is inferred above. From Fig. 3 (c), it is easy to obtain the transition frequency of the single-carrier devices based on sTCTA and eTCTA film. And then, based on the transition frequency, the hole carrier mobility of sTCTA and eTCTA film could be calculated to be 2.1×10^{-5} and 4.3×10^{-5} cm²/(V · s), respectively. Therefore, it could be concluded from the transition frequency with similar magnitude that the hole transport ability of the sTCTA film could be absolutely comparable to the eTCTA one.

3.5. Green OLEDs with TCTA hole transport layer

To further demonstrate the effectiveness of sTCTA in devices, the green OLEDs employing the sTCTA as hole transport layer are successfully fabricated and their electroluminescent performances are studied in detail. The structure of the green devices is shown in Fig. 5 (a). The hole injection layer and electron transport layer is PEDOT:PSS and Bphen, respectively, and the EML is the CBP doped with 10 wt% lr(ppy)₃. For comparison, the green OLED employing eTCTA as hole transport layer is also fabricated.

The green OLED with sTCTA exhibits excellent electroluminescent properties as well as the one based on eTCTA and even performs better tolerance to high bias voltages. The current densityvoltage-luminance and current efficiency-luminance-power efficiency characteristics are shown in Fig. 5 (b) and (c). The turn-on voltage of the sTCTA and eTCTA devices is about 3.4 and 3.2 V, respectively. Additionally, the current density of sTCTA device is almost identical to that of eTCTA device when the bias voltage is over 5 V, indicating the equally efficient transporting properties of sTCTA in the devices. Nevertheless, compared with eTCTA device, the current density of sTCTA device is much lower under the low bias voltage. Since there is no obvious difference between sTCTA and eTCTA device in the luminance at low bias voltage, the lower current density of sTCTA device should be attributed to the decrease of leakage current caused by the smoother and denser USC sTCTA film. Besides, the range of operating voltage for sTCTA device is much wider than that for eTCTA device, resulting in that the luminance of sTCTA device could attain to 63065 cd/m² while the maximum luminance of eTCTA device is only 35428 cd/m². The higher tolerance of sTCTA device to high bias voltage should be the superiority induced by better uniformity of USC sTCTA film and the subsequent organic films deposited on it. With regard to the performance in efficiency, either power efficiency or current efficiency of the sTCTA devices is almost identical with those of the eTCTA devices. Additionally, due to the decrease of the leakage current at low bias voltages, the maximum efficiency of sTCTA device is even a little better than those of eTCTA device. As indicated in Fig. 5 (c), the maximum power, current and external quantum efficiency of sTCTA device is 43.2 lm/W, 70.0 cd/A and 19.9%, respectively, while the maximum power, current and external quantum efficiency of eTCTA device is 35.7 lm/W, 68.9 cd/A and 19.8%, respectively.

Furthermore, the introducing of sTCTA film in OLEDs won't affect the emission spectra and color stability of the devices as well. The normalized emission spectra of sTCTA and eTCTA devices at the luminance of 1000 cd/m² are shown in Fig. 6 (a). The sTCTA and eTCTA devices both exhibit intrinsic emission of $Ir(ppy)_3$ with a peak wavelength of 514 nm, proving the efficient exciton blocking effect of sTCTA and eTCTA film. Additionally, the normalized emission spectra of sTCTA device with different luminance are also



Fig. 5. The (a) structure of the green OLEDs employing TCTA as hole transport layer, (b) current density-voltage-luminance and (c) current efficiency-luminance-power efficiency characteristics of green OLEDs employing TCTA film as hole transport layer and the inset is their external quantum efficiency (EQE) characteristics.



Fig. 6. The (a) normalized EL spectra of green OLEDs employing sTCTA and eTCTA film as hole transport layer at 1000 cd/m², (b) normalized EL spectra of green OLEDs based on sTCTA film at different luminance, (c) (e) and (d) (f) spectral distribution of green OLEDs based on sTCTA and eTCTA film at different voltage or viewing angle.

shown in Fig. 6 (b). It can be seen that the emission spectra of sTCTA device has no significant change with the luminance. When the luminance increases from 100 cd/m² to 40000 cd/m², the CIE coordinates of the sTCTA device just change from (0.281, 0.641) to (0.291, 0.638). Besides, from the spectra distribution of the devices at different voltage and viewing angle shown in Fig. 6 (c)–(f), it can be seen that whether bias voltage or viewing angle changes, the sTCTA device exhibits excellent stability behavior in spectra distribution just as well as the eTCTA device. Therefore, the excellent color stability could also be obtained in the devices based on USC hole transport layer.

4. Conclusion

In summary, high quality TCTA film is successfully realized by the ultrasonic spray coating process, showing the feasibility of this process in fabricating nanoscale small molecular organic thin film. The USC-TCTA film doesn't show obvious difference on optical properties and hole transport properties with the VTE one. Besides, the USC-TCTA and the subsequent organic films deposited on it even exhibit more uniform surface topography, indicating the superiority of liquid-phase growth in film quality. The effectiveness of USC-TCTA in OLEDs is also demonstrated since the green OLEDs employing USC-TCTA film as hole transport layer exhibit excellent electroluminescent performances. The introducing of USC-TCTA film could still ensure the green OLEDs possess low turn-on voltage, high current and power efficiency that could attain to 3.4 V, 70 cd/A and 43.2 lm/W, respectively, confirming the efficient hole transport and exciton blocking ability of the USC-TCTA film. Additionally, the higher tolerance to high bias voltage caused by the smoother and denser USC-TCTA film could make the devices possess a maximum luminance of 63065 cd/m², which is much higher than that of devices based on VTE-TCTA film. This work may be beneficial to the realization of low-cost small molecular OLEDs.

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