Free-standing film electronics using photo-crosslinking layer-by-layer assembly†

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A robust and efficient strategy for preparing a substrate for highly flexible and patchable electronics was developed *via* a photo-crosslinking LbL spin-coating process that allows various thicknesses to be achieved without any rinsing or intermediate purification steps.

In designing organic-based devices, such as organic thin-film transistors (OTFT),[1] solar cells,[2] organic light emitting diodes (OLED),[3] and others, the current trend is to improve flexibility as well as to maximize performance by the use of simple processes. To improve flexibility after device fabrication, significant efforts have focused on free-standing polymeric or nanocomposite films produced by using various approaches, including the sol–gel process, the self-assembly of block copolymers or layer-by-layer (LbL) assembly.[4–9] However, the applications of these films have been limited to the preparation of membranes, sensors and mechanically reinforced nanocomposite films.[4,6,7,9] In all of these studies, the free-standing films were obtained by physically detaching or by dissolving inserted sacrificial thin layers from the supporting substrates. This process remains a challenge in the fabrication of flexible devices with electrical properties due to surface waviness and physical damage.

Free-standing films have been extensively studied as LbL-assembled multilayers. The traditional LbL assembly method[4–7,10–17] is the most versatile for preparing ultrathin films as it allows the tailored nanoscale preparation of films, and the composition allows functionality through complementary interactions between adjacent layers. However, it should be noted that the conventional LbL method is subject to several inherent limitations. First, it is not practical to scale up the layer thickness beyond 10 nm in a single deposition step. For example, in fabricating functional multilayer films on a micron scale, these films consist of hundreds of layers because any layer adsorbed during a single deposition step is only a few nanometres thick after rinsing. Second, it is not possible to consecutively deposit hydrophobic layers without complementary interactions occurring between layers. Third, although LbL hydrophilic multilayers formed onto a sacrificial layer can be separated from the substrates, such an approach can cause physical or chemical damage to the free-standing films unless remarkable precautions are taken.

Herein, we introduce a versatile and simple approach for preparing a substrate for highly flexible and patchable electronics based on LbL free-standing multilayers with highly improved surface quality. Hydrophobic polymers containing UV cross-linkable units were designed for the deposition of multilayers onto sacrificial ionic substrates. These polymers can be deposited consecutively with various thicknesses *via* photo-crosslinking without any rinsing step. A film having a controlled thickness can retain flexibility with excellent surface smoothness (<1 nm) as well as retain enough mechanical strength to produce a free-standing film. This can't be achieved by using other conventional approaches such as spin coating or dip coating. Subsequently, organic thin-film transistors (OTFTs) were fabricated onto the multilayer-coated ionic substrates. Considering that ionic substrates are easily dissolved in water, our approach is simpler, faster and more versatile for the preparation of highly flexible and patchable electronics with controlled flexibility (Fig. 1).

Another significance of our work lies in the fact that our process is completely compatible with current commercialized deposition methods such as sputtering, evaporation and spin coating. In addition, this free-standing multilayer has macroscopically defect-free uniformity, which influences the performance of OTFTs. Therefore,

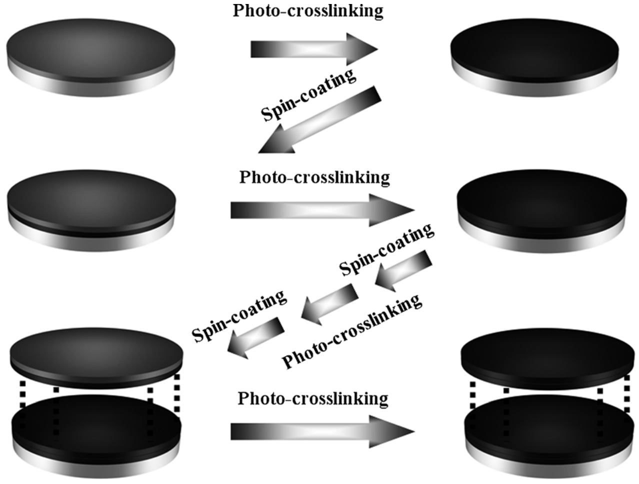

Fig. 1 A schematic of the preparation of multilayers based on photo-crosslinkable polymers.

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our work highlights the fact that direct application of free-standing films with functional multilayers to current electronic devices is feasible without perturbing the nature of the devices.

For the preparation of photo-crosslinkable polymers[18] ($PS-N_3$), experimental details are given in the ESI (Fig. S1).† On the basis of crosslinking reactions, we first investigated the vertical growth of $PS-N_3$ multilayers onto silicon substrates by increasing the layer number as a function of solution concentration. The spinning speed was fixed at 3000 rpm. In this case, the layer thicknesses were increased from 1.6 nm to 250 nm (for $PS-N_3$) (see ESI, Fig. S2).† These thicknesses can be controlled over a broader range by varying the solution concentration or by varying the spinning speed.[19] On the other hand, in the case of the conventional LbL method, which is based on complementary interactions, it is difficult to increase the layer thickness up to tens of nanometres because the washing process removes weakly adsorbed layers.

These crosslinkable polymers can be consecutively deposited onto sacrificial ionic substrates through repetitive photo-crosslinking and spin coating.

In addition, the patterned metal electrodes can be fabricated onto the multilayer-coated ionic substrates by using conventional sputtering or evaporation processes. Films with patterned metal electrodes can be easily separated after dissolving the substrates in water. Based on this strategy, the patterned structures of 500 and 100 μm dot size were prepared onto detachable $(PS-N_3)_{27}$ multilayers by using Pt sputtering, as shown in Fig. 2. Stable adhesion between the metal electrodes and $PS-N_3$ multilayers is formed due to the presence of nitrogen atoms within the multilayers. These films are highly flexible because the total thicknesses of the $(PS-N_3)_{27}$ multilayers are only 4 μm. The flexibility of these films can be further controlled by tuning the deposited layer number (n). Additionally, the mechanical properties of $PS-N_3$ ($M_n = 28$ K/mol) and pure PS ($M_n = 26$ K/mol) films have been measured by using depth-sensing indentation experiments. In this case, it was found that the mechanical properties of 200 nm thick $PS-N_3$ (*e.g.*, elastic modulus = 4.53 GPa and hardness = 0.61 GPa) were similar to those of PS films (*e.g.*, elastic modulus = 4.35 GPa and hardness = 0.51 GPa). Although we did not investigate the minimum thickness of free-standing LbL films, the thickness of free-standing films could be successfully decreased to about 1 μm.

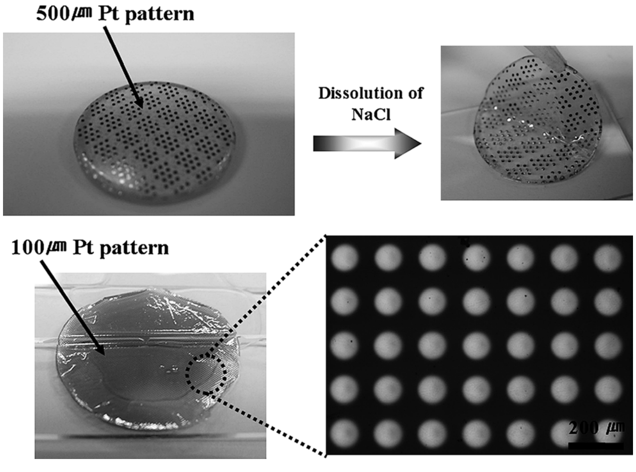

Fig. 2 Photographs of $PS-N_3$ multilayers with dot patterns of 500 μm and 100 μm prepared by using Pt sputtering. The Pt electrodes were patterned onto the $PS-N_3$ multilayer-coated NaCl substrates by using a shadow mask followed by consecutive removal of NaCl, which produces the highly flexible free-standing films with patterned features.

These results suggest that various electronics can be produced onto free-standing multilayer films by using sacrificial ionic substrates. Since $PS-N_3$ multilayers have highly uniform and smooth surfaces (average the peak to valley distance (Δz) of about 1 nm), they are applicable to various electronic film devices that require an extremely smooth surface (see ESI, Fig. S3a†). It should be noted that the commercialized poly(ethylene terephtalate) (PET) substrates widely used for flexible electronics have a relatively high surface roughness (Δz about 25 nm) (see ESI, Fig. S3b†) and thus the resulting morphology of the deposited materials might significantly deteriorate and influence the device's performance.[20] In addition, it is difficult to apply such commercialized films with low flexibility (above 80 μm thickness) to wearable or patchable electronics requiring high flexibility.

Based on these results, we fabricated flexible OTFTs as shown in Fig. 3a. The Al gate electrode, poly(4-vinylphenol) (PVP) for the polymer gate insulator, pentacene for the active semiconducting layer, Al source/drain electrodes onto $PS-N_3$ multilayer-coated NaCl substrates as shown in Fig. 3a. Removing the NaCl substrates yielded highly uniform, transparent and flexible OTFTs (Fig. 3b). It is noteworthy that these transparent film devices can be reversibly pasted on and then detached from various surfaces by using a glue coating. Furthermore, their flexibility could be easily controlled by altering the number of deposited layers. Also, we investigated the electrical properties of free-standing electronics. Fig. 4a–c shows the transfer, output and mobility characteristics of 4 μm $PS-N_3$-based OTFTs onto NaCl, and the free-standing $PS-N_3$ multilayer-based OTFTs. The ratio of the channel width to length was 1000: 150 μm. In this case, the on/off current ratios of about 1.03×10^3 (for the

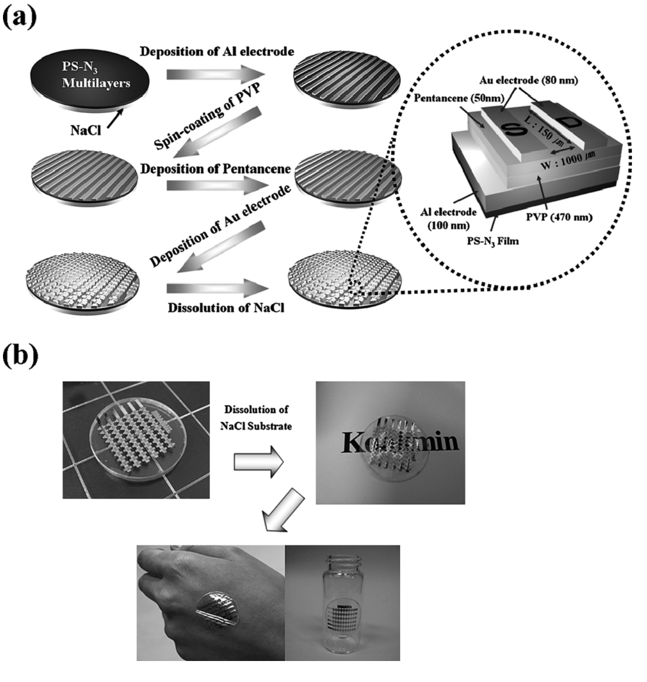

Fig. 3 (a) A schematic for the preparation of free-standing electronic films. Photographs of transparent highly flexible and patchable OTFTs produced by using (b) $PS-N_3$ multilayers (4 μm thickness). The OTFT films could be pasted on curved glass and the back of one's hand by using glue.

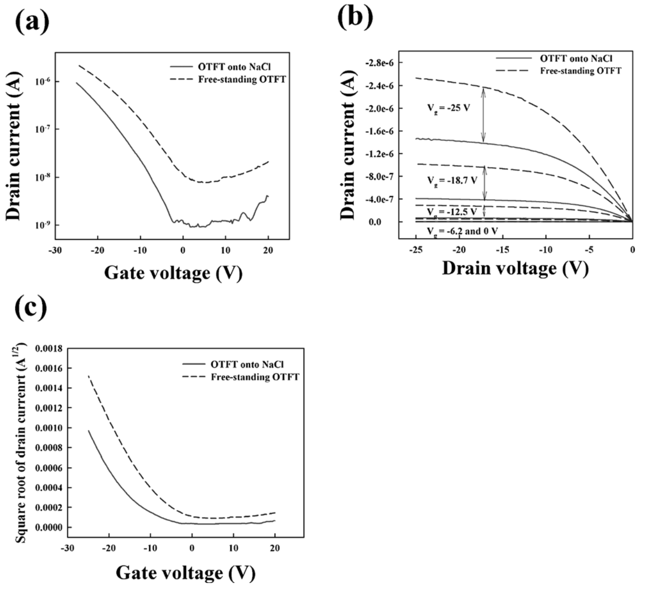

Fig. 4 (a) Transfer, (b) output and (c) $ID^{0.5}$–Vg characteristics of PS-N_3 multilayer-based OTFT onto NaCl and free-standing PS-N_3 multilayer-based OTFT. The field-effect mobility, threshold voltage and on/off drain current ratio of OTFT onto NaCl were 0.181 $cm^2 V^{-1} S^{-1}$, −11.4 V and 1.03×10^3, respectively. The field-effect mobility, threshold voltage and on/off drain current ratio of the free-standing OTFT were 0.222 $cm^2 V^{-1} S^{-1}$, −5.7 V and 2.84×10^2, respectively.

device fabricated onto the NaCl substrate) and 2.84×10^2 (for the free-standing device) and the off currents of about 1×10^{-9} A (NaCl) and about 1×10^{-8} A (free-standing) were achieved. In addition, it was observed that the drain current of the free-standing OTFT was slightly higher than that of the NaCl OTFT. This observation is supported by the possibility that the reduced strains, after the formation of free-standing film, can increase the packing density of pentacene. Actually, in the bending of an OTFT, the performance is aggravated by strain effects.[21] As a result, these phenomena lead to a decreased threshold voltage (NaCl OTFT, $V_{th} = -11.4$ V; free-standing OTFT, $V_{th} = -5.7$ V) and an increased field-effect mobility (NaCl OTFT, $\mu = 0.181$ cm²/V s; free-standing OTFT, $\mu = 0.222$ cm²/V s). The device performance will be further improved if well-known functional materials, such as octadecyltrichlorosilane for pentacene growth and optimized processing conditions,[22–25] are used.

In summary, we demonstrated a robust and efficient fabrication strategy for a substrate for highly flexible and patchable electronics based on free-standing multilayers. Unlike the conventional LbL process, the photo-crosslinking of each layer allows a wide range of thicknesses to be achieved without any additional steps such as thermal annealing at high temperature, rinsing or intermediate purification. The resulting multilayers are mechanically and chemically stable, and are highly compatible with commercialized deposition processes such as evaporation, sputtering or spin coating. The deposition of various metal electrodes and semiconducting materials onto multilayer-coated ionic substrates produced highly flexible and patchable electronic devices without buckling or waviness in the film's morphology. Our approach opens new possibilities for the fabrication of highly flexible and patchable electronic applications.

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