Fingerprint Recognition

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A Release-Induced Response for the Rapid Recognition of Latent Fingerprints and Formation of Inkjet-Printed Patterns**

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Fingerprints are widely used for personal identification in numerous fields,[1] such as forensic investigation,[2,3] law enforcement,[4] access control,[5] or medical diagnostics.[6] A latent fingerprint, an impression of the ridge pattern of a human finger, is formed on a surface when a finger touches the surface, and it is usually invisible in daylight. Various elegant physical (powder dusting, small particle reagent, metal deposition), chemical (iodine, cyanoacrylate, ninhydrin, and their analogues), spectroscopic (laser, fluorescence, mass spectrometry, and UV/Vis and infrared absorption), and combination techniques have been explored for the visualization or enhancement of latent fingerprints (LFPs) under specific circumstances.[7,8] Among those reported, several efforts for intelligent LFPs detection are of particular interest. Russell and co-workers devised a smart combined route to simultaneously identify drug metabolites and fingerprints based on antibody-functionalized nanoparticle deposition.[6,9] They also demonstrated that antibody–magnetic-particle conjugates can be applied to the fast imaging of LFPs within 15 min.[10] Almog et al. employed the natural product genipin as a safer and benign reagent to develop LFPs with both color and fluorescence.[11] A nondestructive example of fluorescence imaging was reported recently in which LFPs were successfully transferred to a fluorescent conjugated polymer film.[12] Despite amazing achievements that have been made in LFPs recognition, it is still a great challenge to develop LFPs in a technically simple, rapid, and easy handling way. To this end, we demonstrate herein a new easy-to-perform and versatile strategy that enables ultrafast identification of LFPs on various surfaces by using commercial thermoplastic polyurethane (TPU) resin and an electrospinning technique with a release-induced response (RIR) process.

The nondestructive collection and identification of LFPs on various surfaces were carried out using an electrospun TPU/fluorescein nanofiber mat. LFPs on various surfaces were transferred easily onto the electrospun mat by softly pressing the mat on the surfaces, and then these LFPs were immediately visualized (30 s) in red under daylight after exposing the mat to hot air (100 °C). This relatively simple method overcomes the disadvantages in most current LFP detection techniques, which usually require laborious pre-/post-treatments, suffer from contaminative reagents (liquids, powders, and chemical fuming), or involve various sophisticated spectroscopic instruments. The approach offers the advantage that the identification of LFPs can be easily achieved within seconds under daylight. Also, this portable electrospun mat is a valuable tool for fingerprint examiners that allows them to rapidly, facilely, and nondestructively lift fingerprints from various surfaces without pre-treating fingerprints. We also show that this phenomenon can be ascribed to a typical release-induced response (RIR) process. A cross-linking behavior exists between TPU and the residues of fingerprints, which induces phase separation between TPU network and fluorescein. This separation allows fluorescein to be released from TPU nanofibers easily, conferring a color variation. To further validate this RIR mechanism, we also show that the versatile patterns on these electrospun mats can be followed by the RIR procedure and fabricated by a jet printer using water as an "imaging ink", along with tertiary amine catalyst for accelerating cross-linking process. To the best of our knowledge, this is the first example of the utilization of an electrospun mat for the identification of LFPs and formation of inkjet-printed patterns, which may be extended to explore microreactors,[13] multifunctional combined sensors,[14] and also versatile detection/analysis devices.[15]

Figure 1 shows the schematic procedure for fabrication of the sensor mat for fingerprints. The electrospinning technique, a cost-effective and versatile approach for facile generation of fibrous polymer mats with the virtue of large surface area,[16] was employed to prepare a homogeneous blend of TPU and fluorescein with a nanofiber structure (Figure 1 A). Given that TPU is a multiblock copolymer with thermodynamic incompatibility of hard segments and soft segments,[17] a solvent mixture of DMF/THF was chosen to avoid microphase-separated morphology. The resulting homogeneous TPU/fluorescein solution was electrospun into nanofibers that were collected on the surface of a grounded rotating drum to obtain a uniform straw-colored mat (Figure 1 B, inset; Supporting Information, Figure S1–S3, Table S1). A scanning electron microscope (SEM) image of a fresh TPU/fluorescein mat without LFPs shows that the fiber structures in the mat have a highly uniform size distribution with an average diameter of about 300 nm (Figure 1 B). Interestingly, one donor deposited an LFP on the electrospun

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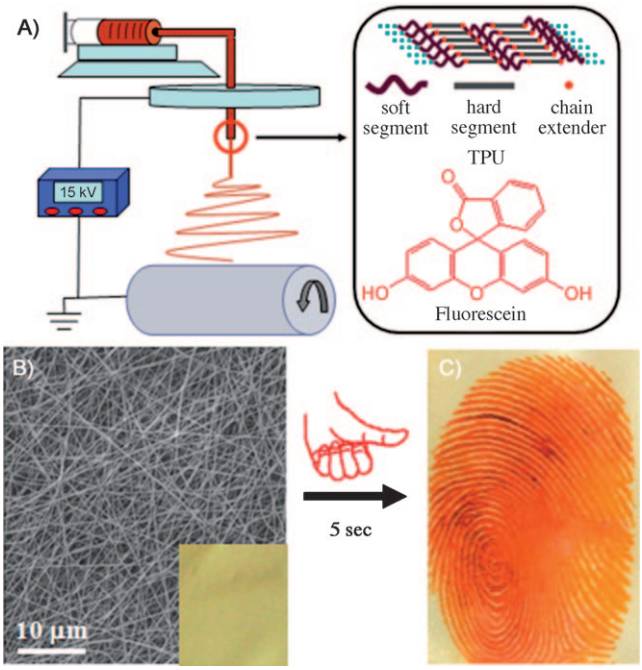

Figure 1. A) Representation of the electrospinning setup using a rotated drum collector. B) SEM image of the TPU/fluorescein composite nanofibers. Inset: A photograph of the mat formed of TPU/fluorescein composite nanofibers. C) Bright-field image of a fingerprint on the electrospun TPU/fluorescein mat that was touched by a finger and then developed with hot air for 5 seconds.

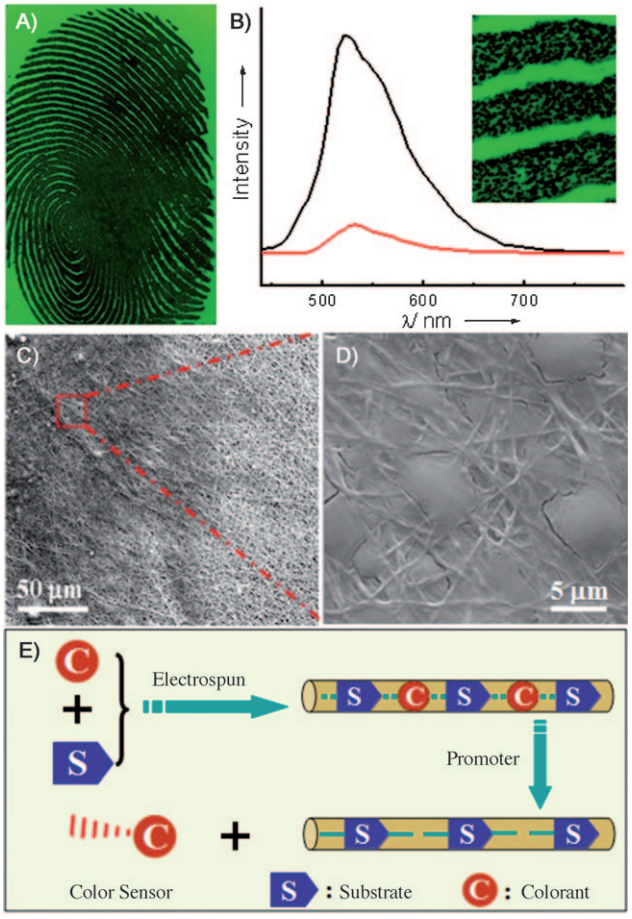

Figure 2. A) Fluorescence image of the fingerprint from Figure 1C. B) Fluorescence emission spectra of furrow domains (black, strong) and ridge domains (red, weak) under excitation at $\lambda_{ex} = 432$ nm. Inset: fluorescence images of a section of the same fingerprint at higher magnification. C) SEM image of a typical transitional zone between ridge and furrow. D) The enlargement SEM image of a ridge area. E) The RIR process.

TPU/fluorescein nanofiber mat, and the LFP would be immediately visualized (less than 5 s) under daylight after exposing the mat to hot air (100 °C, Figure S4). A typical developed fingerprint on the electrospun mat is presented in Figure 1C, where the contact area of the fingerprint ridges displays an obvious change in color to red and the distinct ridge image enables identification of the individual.

We explored the mechanism for the visualization of LFPs in this system. Fluorescence microscope analysis reveals that the fluorescence of the ridge contact areas almost vanishes, whereas that of the furrow contact areas remains unchanged (Figure 2A). The black strings correspond to the red patterns of the bright-field image shown in Figure 1C, both of which give the clear ridge structure of the fingerprint for personal identification. By scrutiny of dark zones (Figure 2B, inset), it can be seen that the ridge areas involve plenty of clusters, which refers to red fluorescein powder released from the electrospun nanofibers. As the fluorescein powder does not exhibit fluorescence (Supporting Information, Figure S5), the release of fluorescein in the ridge zones led to the fluorescence quenching (Figure 2B). SEM measurement was carried out to investigate the micromorphology of the TPU/fluorescein mat with the fingerprint deposition. As shown in the Supporting Information, Figure S6, the regular black and white lines indicate the characteristic ridge and furrow patterns. A typical image of transitional zone between ridge and furrow is displayed in Figure 2C. No morphological variation is found in the furrow domain (right part in Figure 2C); however, a cross-linked structure occurs in the ridge area (left part in Figure 2C; Figure 2D). The residues of fingerprints (that is, sweat, including water, amines, amino acids, etc.[18]) are reactive towards traces of the free isocyanate group in TPU,[19] and can also induce hydrolysis of polyester-based TPU,[20] which should be responsible for the cross-linking of TPU nanofibers. Specifically, a ridge zone involves thousands of electrospun nanofibers with the merit of high surface area, which facilitates rapid and sufficient mass exchange between the TPU nanofibers and surrounding sweat to produce numerous knots and hence could induce the effective release of fluorescein from the nanofibers. We noted that the TPU/fluorescein film without any micro/nanostructure prepared by the spin-coating method could not develop a clear fingerprint pattern.

In a further experiment at room temperature, the electrospun mat with prior repeated treatment by palms also shows a cross-linked network structure within four days and a color change from straw-colored to red, along with fluorescence quenching over 30 days (Supporting Information, Figures S7, S8). This time-dependent behavior indicates that the

fluorescein is gently released from the nanofibers after depositing the prints, while the process will be remarkably accelerated by heating. In addition, no color, fluorescence, or morphology change could be observed when the electrospun mat was treated by gloved fingers, which confirms that the sweat of the volunteer's fingers initiates the changes in the mat surface.

The above investigations suggest that the development of LFPs on the TPU/fluorescein nanofiber mat is based on a RIR process (Figure 2E). The sensor mat for fingerprints involves fluorescein for color contrast, just like previous detection means in which fingerprints were examined based on visible contrast between prints and background.[21] The mat of the homogeneous blend of TPU (substrate) and fluorescein (colorant) is obtained with nanofiber structure by using the electrospinning technique. When a finger touches the mat, sweat (promoter) deposited on the ridge areas is transferred to the surface of the mat, inducing the cross-linking process of TPU nanofibers. The blend in the contact area is then unstable, resulting in the phase separation of the blend and release of fluorescein through which the LFP is visualized.

It is of practical importance to achieve the rapid identification of LFPs on various surfaces, so the applicability of this platform technology for the detection of LFPs on different surfaces was assessed (Figure 3A). First, LFPs were randomly deposited on various clean surfaces by volunteers. Subsequently, LFPs were successfully transferred onto the electrospun mats by softly pressing the mat on the surfaces. Finally, the electrospun mats with fingerprint deposition were developed by heating with hot air (100 °C) in 30 seconds to directly visualize LFPs in red. The virtue of large specific surface area for the mat guarantees the successful collection and ultrafast high-resolution identification of LFPs from various surfaces. As shown in Figure 3B–G, all fingerprint images transferred from quartz, glass, stainless steel, polypropylene film, marble, and wood show clear ridge details that would enable personal identification. Several nondestructive transfer and detection routes have been presented very recently in which the fingerprints can be lifted from specific surfaces and then developed by complicated optical means such as ATR-FT-IR or fluorescence spectroscopic imaging.[7d,12] Our work offers major advantages that LFPs can be nondestructively transferred from various surfaces, easily developed, and quickly distinguished under daylight, which is suited to on-site and real-time detection of LFPs.

To further validate the RIR process, we constructed versatile patterns on the TPU/fluorescein electrospun mats by an inkjet printer with the use of water as an "imaging ink". Given that inkjet printers can precisely monitor chemical targets by a computer system,[22] it was employed to accurately eject chemicals to a pre-defined position on the TPU/fluorescein mat. As shown in Figure 4A, when a signal is given, the piezoelectric cell changes shape, which generates a pressure pulse in the fluid forcing a droplet of analyte solution from the orifice onto the mat. The interaction between electrospun nanofibers and analyte occurs during the procedure, resulting in the release of fluorescein from the electrospun mat to form the patterned images. In this work, a mixture (denoted as A-1) of 70 wt% bis(2-dimethylaminoethyl)ether (BDMAEE; **1**) and 30 wt% diisopropylene glycol (DPG; **2**) was chosen to boost the cross-linking of TPU fibers

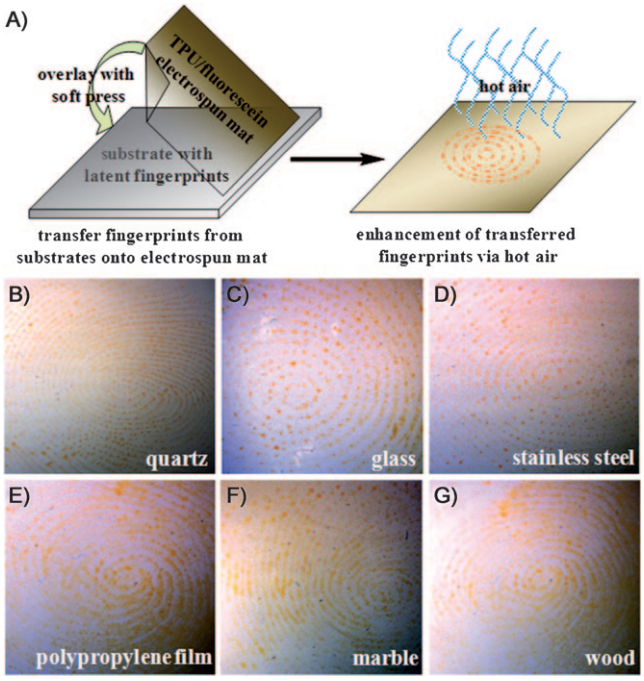

Figure 3. A) The process for imaging latent fingerprints on various surfaces using the electrospun TPU/fluorescein mat. B–G) Bright-field images of segmental fingerprints on various indicated surfaces obtained after heat treatment (100 °C hot air) for up to 30 seconds.

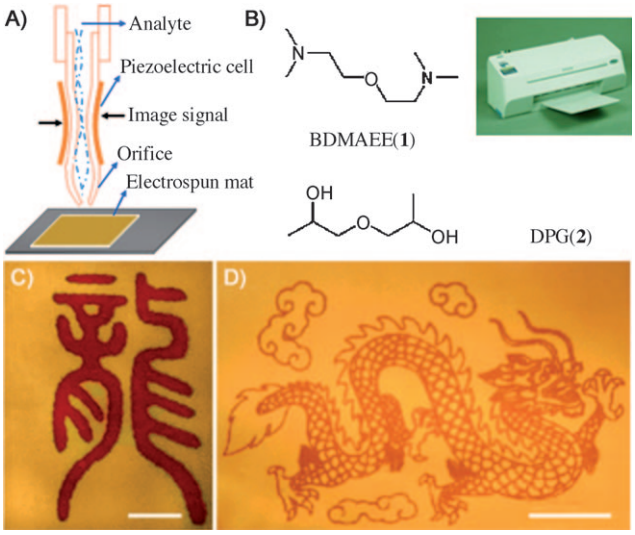

Figure 4. A) Perspective view of the piezoelectric inkjet printer head. B) Structures of BDMAEE and DPG. Inset: A photograph of an Epson ME 30 inkjet printer. C, D) Photographs of patterns that were printed on the electrospun TPU/fluorescein mat using an aqueous solution of A-1 as printing ink: C) A Chinese word for dragon in a seal script style (scale bar: 5 mm) and D) a typical of Chinese dragon pattern (scale bar: 1 cm).

and hence the release of fluorescein (Figure 4B). A-1 was diluted 100-fold in water and injected into vacant and intact cartridges of a jet printer (Figure 4B inset). A Chinese word for dragon in a seal script style was printed on the TPU/fluorescein mat (Figure 4C). The corresponding image of a Chinese dragon, which represents wealth, power, and good luck, was also printed with high resolution (Figure 4D). In turn, this patterning procedure confirms the RIR mechanism for the visualization of LFPs we proposed above. Moreover, as inkjet printing technology is a versatile tool for accurately delivering very small volume of liquid samples, it is anticipated that the combination of inkjet printing and this RIR process could be extended to exactly explore devices for electronic and biomedical applications.

In summary, a novel method of a RIR process for the ultrafast recognition of LFPs on various surfaces has been demonstrated for the first time that is based on an electrospun nanofiber mat. Encouragingly, compared with classical methods, this approach shows the unique advance that LFPs can be nondestructively lifted from various surfaces, easily developed within 30 seconds, and distinguished under daylight. This electrospun mat can also be utilized in fabricating versatile inkjet-printed patterns with water as the imaging ink, and thus might be adapted for more practice applications, for instance, in sensors, microreactors, and medical systems.

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