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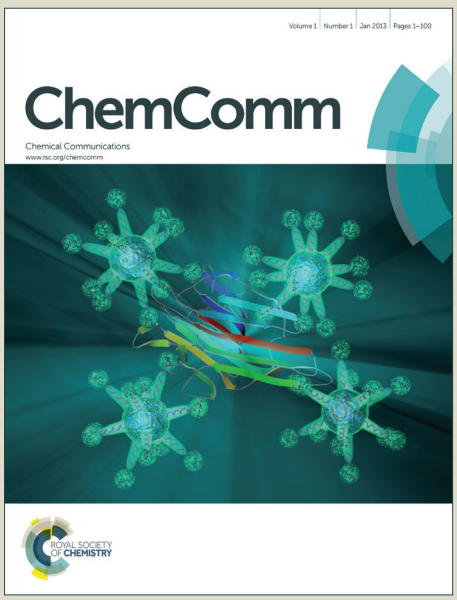

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Sweat Pore Mapping Using a Fluorescein-Polymer Composite Film for Fingerprint Analysis

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A simple but efficient sweat pore mapping method based on a fluorescein-PVP composite film was developed for fingerprint analysis. The composite film displays a fluorometric turn-on response upon contact with a small quantity of water secreted from human sweat pores, allowing precise mapping of sweat pores on a fingertip.

Every individual has unique ridge patterns on their fingertips and the patterns comprised of sweat components (fatty acids, amino acids, inorganic salts, etc.) are transferred to a solid substrate when a finger touches the surface. Analyses of the latent fingerprints on the solid surface have been, without a doubt, one of the most reliable sources of evidence for proving an individual's presence in a specific environment.[1,2] Accordingly, a variety of techniques have been developed for imaging the latent fingerprints, including physical (powder dusting, metal deposition, etc.),[3,4] chemical (ninhydrin, cyanoacrylate, conjugated polymer, etc.),[5,-10] biochemical (antibody, aptamer, etc.),[11-15] electrochemical,[16-20] and spectroscopic approaches.[4,21-23] Regardless of the reagents and delivery methods, researchers/investigators have devoted their efforts to obtaining clear friction ridge structures from the latent fingermarks. Because the current fingerprint database has been constructed using conventional inking methods or low resolution digital scanners, only information regarding ridge patterns have been stored.

Fingermarks deposited on a porous substrate such as paper often are obtained as dot images or mixed dot/ridge images after development instead of pure ridge patterns. This is due to the highly networked structures of paper that limit free migration of nonvolatile sweat components. The dot images have been vastly neglected as evidence owing to the fact that the pore images do not have matches in currently data-based ridge patterns. Accordingly, the advent of rapid and reliable pore mapping technologies would lead to methods that can be used cooperatively and/or independently to discriminate/define human identities.[24] The reason for this lies in the fact that pores on fingertips are permanent, immutable and unique.[24] Although high resolution scanners enable imaging of the sweat pores on fingertips, they are expensive and require complicated software for the extraction of pore information.[25,26] In addition, scanners often produce false information owing to the presence of complicated ridge and pore structures.[25,26]

The limitations associated with current fingerprint analysis technologies have led us to explore new methods for mapping sweat pores on fingertips. Recently, we described a sweat pore mapping strategy that utilizes hydrochromic polydiacetylene (PDA) films.[27] We observed that deposition of fingermarks on a hygroscopic PDA film leads to a water promoted colorimetric response that can be used to map sweat pores. However, this effort requires tedious screening of diacetylene monomers and hygroscopic elements to achieve suitable sensitivity for sweat pore mapping. In addition, the majority of hydrochromic PDA films undergo a blue-to-red color transition in humid environments (relative humidity >80%) prior to fingerprint deposition. Furthermore, most of the diacetylene monomers are expensive and their mass production required for practical use is limited. In a more recent investigation described below, we devised a new strategy for mapping sweat pores on fingertips. The method utilizes a system composed of water-responsive fluorescein and a hydrophilic matrix polymer (i.e., polyvinylpyrrolidone, PVP). The cost-effective fluorescein-PVP film enables excellent mapping of sweat pores under a wide humidity range (20-90%, relative humidity).

Fluorescein, a readily available small molecule dye, undergoes an equilibrium process involving interconversion of a ring-closed spirolactone and a ring-opened fluorone form (Fig. 1a). Ring-closed fluorescein is nonfluorescent while the ring-opened form strongly fluoresces. In the presence of water, the equilibrium process favors the ring-open form, which is demonstrated by observing a significantly enhanced fluorescence emission upon exposure of a fluorescein-polymer film to water (Fig. 1b). We envisioned that if small amounts of water secreted from sweat pores on fingertips, captured by a matrix comprised of hydrophilic polyvinylpyrrolidone (PVP) polymer, facilitate the ring opening process, fluorescence imaging of sweat pores would be possible.

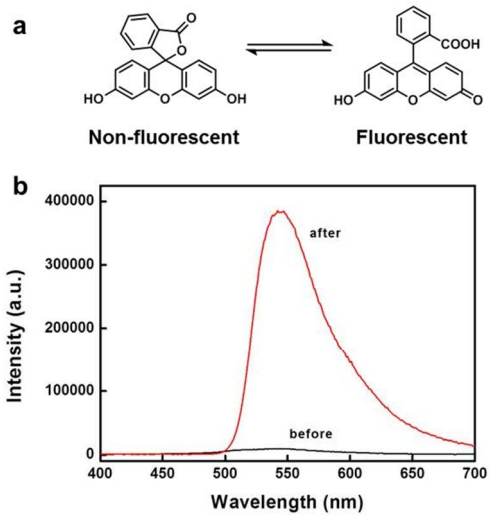

Fig. 1 (a) Equilibrium of fluorescein between ring-closed nonfluorescent spiro-lactone form and ring-opened fluorescent fluorone form. (b) Fluorescence spectra of a fluorescein-PVP film before (black line) and after (red line) exposure to water.

In accord with this expectation, green fluorescent dot patterns were observed using fluorescence microscopy when a fingermark is deposited on a 2% fluorescein-PVP composite film (wt%, thickness: ~ 40 μm) (Fig. 2). This finding suggests that the small amount of water secreted from sweat pores in contacted areas penetrates into the composite film where it causes a turn-on of fluorescence emission.

To demonstrate that the fluorescence microdots correspond to sweat pores, the fluorescent image was superimposed on a digitally scanned fingertip image. As can be seen by inspecting the superimposed images (Fig. 3), the positions of the black microdots, obtained using digital scanning and corresponding to pores on fingertip ridges, match those of fluorescent microdots. Notably, the observation that some of pores are not superimposed on the fluorescent microdots indicates the presence of inactive pores that do not secret sweat at the time of fingerprinting (orange circles in Fig. 3). Thus, the fluorescein-PVP composite film enables colorimetric differentiation between the sweat-secreting active pores and inactive pores.

For practical applications, the sensor film should have a balanced sensitivity so that it does not undergo an emission transition under ambient conditions. However, it should be sufficiently sensitive to respond to trace amounts of water in sweat. In fact, many previously described hydrochromic materials are either too sensitive for this purpose or they are not noticeably responsive to sweat (Table S1, ESI†). Fortunately, the fluorescein-PVP composite film does not undergo significant fluorescence changes under ambient conditions, whereas it is sufficiently responsive to display a fluorometric transition upon contact with small amounts of water secreted from sweat pores (Fig. S1, ESI†). One meritorious feature of the fluorescein-PVP fingerprinting system is that the sensor film can be used for pore mapping even after exposure of the film to an environment of 100% relative humidity. Clean sweat pore maps were obtained with the high humidity-exposed films by a brief heat treatment (60 °C, 3 min) of the films (Fig. S2, ESI†). Also, the water-activated fluorescence was found to persist for sufficient time periods (< 9 days) under ambient conditions (Fig. S3, ESI†). The moderate sensitivity and the long-term emission properties indicate that the fluorescein-PVP composite film is ideal for sweat pore mapping applications.

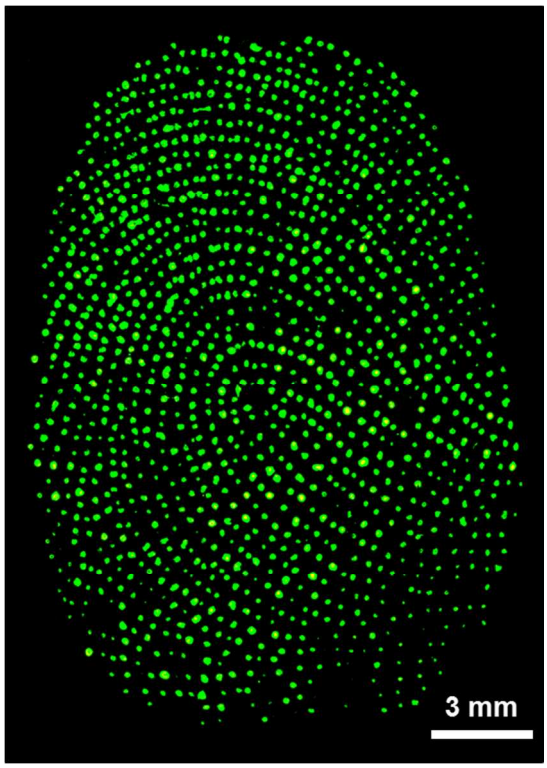

Fig. 2 Contrast-enhanced fluorescence image of a sweat pore pattern mapped on the fluorescein-PVP composite film.

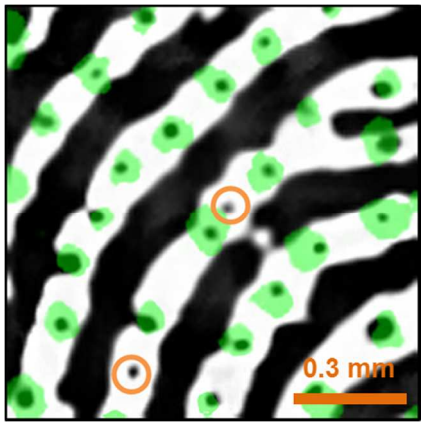

Fig. 3 Superimposed image of the fluorescence sweat pores (green dots) on a scanned fingerprint digital image. The black dots inside the orange circles indicate pores that do not secret sweat.

In order to demonstrate the fluorescein-PVP composite films sensing water among sweat components, we prepared several aqueous solutions containing water only, salt in water, water containing amino acids, and artificial sweat (Fig. S4, ESI†).[28,29] A small amount of each solution

was gently placed on the composite film using a tappered glass capillary before carrying out fluorescence analysis. The results show that fluorescence caused by application of the test solutions all have approximately the same intensity (Fig. S4, ESI†), indicating that fluorescence emission of the composite film is due to the presence of water.

To further understand the mechanism of the water-activated fluorescence of the fluorescein molecules, we prepared a film, composed of PVP and fluorescein diacetate, which does not undergo the water-promoted ring-opening reaction. This film does not display an emission response to sweat-pores (data not shown). This result demonstrates the proposed mechanism; that is, the ring-opening reaction of the fluorescein molecules in the presence of water induces the fluorescence emission.

The significance of using the hydrophilic matrix polymer PVP was demonstrated by the observation that no sweat pore patterns arise when fingermarks are deposited on fluorescein containing polymer composite films derived from hydrophobic polystyrene (PS) and polymethyl methacryate (PMMA) (Fig. S5, ESI†). In contrast, sweat pore mapping is successful when the hydrophilic polyacrylic acid (PAA) matrix is employed. However, because the fluorescein-PAA film is also strongly emissive prior to fingermark deposition, poor sweat pore images are generated (Fig. S5, ESI†). A study of the effect of the amount of fluorescein in the fluorescein-PVP film on the quality of the sweat pore map showed that reliable images are obtained when the fluorescein content is in the range of 0.1-10 wt% relative to the matrix polymer (Fig. S6, ESI†).

In the final phase of this investigation, the new sweat pore mapping method based on the fluorescein-PVP composite film was applied to latent fingerprint analysis. A fingerprint pattern of a fluorescent microscope image was deposited on the fluorescein-PVP film (Fig. 4a) along with a latent sweat pore image, obtained from the same individual using a modified ninhydrin staining method (Fig. 4b).[1,30] Image analysis software (ImageJ) was then used to determine the pore positions in each image. To discriminate between the sweat pore patterns of the two images, we employed a pore-pattern-matching program implemented in MATLAB (see the detailed process for the image analysis and the pattern-matching program in reference[27]). Analysis of the red dots shown in the images displayed in Fig. 4a,b, which correspond to matching points between the two images, shows that the sweat pore patterns generated by using both methods are in excellent agreement. A visual comparison of the image (Fig. 4e), obtained by superimposing the magnified boxed areas in Fig. 4c and Fig. 4d, further demonstrates the reliability of the pore-matching program. To evaluate the reliability of the new sweat pore mapping process, the same procedure described above was utilized to produce fluorescence and latent images from five individuals. Subsequent application of the pore-pattern-matching process demonstrated that the patterns deposited by these individuals can be readily distinguished (Fig. S7, ESI†).

In conclusion, in the effort described above we have designed and developed a simple but efficient and reliable sweat pore mapping method based on a fluorescein-PVP composite film. The composite film displays a fluorometric turn-on response upon contact with a small quantity of water secreted from human sweat pores in which each pore is reflected in a discrete fluorescence microdot. Using an image analysis tool, the coordinates of the microdots can be extracted and the patterns can be exploited for personal identification applications. The pore-pattern-matching process used in this study serves as an excellent method to unveil the relationship between the fluorescence sweat pore patterns and latent fingerprints obtained from the same individual. An important feature of the new method is that all of the materials for film fabrication are commercially available and can be used without any chemical modification. As a result, mass production using a standardized industrial manufacturing process is feasible. Importantly, we believe that the new sweat-pore-based identification system has potential applications to identifying individuals in situations related to criminal investigations, licence validations, and biometric security applications.

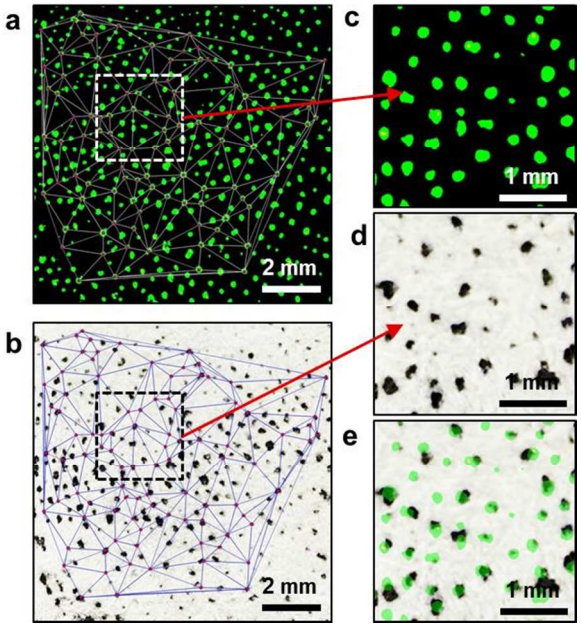

Fig. 4 (a,b) Contrast-adjusted fluorescence microscope fingerprint image printed on a fluorescein-PVP film (a) and a latent image of the same fingerprint developed with ninhydrin (b). The red colored dots, obtained from the image matching process, indicate the matching points between the two images. (c,d) Magnified images of marked areas in (a) and (b). (e) Superimposed image of (c) and (d). The latent fingerprint image shown in (b) was obtained by pressing a fingertip on an unmodified paper followed by staining with ninhydrin. The original purple colored dots obtained from ninhydrin staining were transformed to black colored dots using a Photoshop program because overlapping the green colored fluorescence image (c) with the black colored dots (d) results in a better superimposed image (e).

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Notes and references

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