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Fingerprint imaging by scanning electrochemical microscopy

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Abstract

An efficient strategy for visualizing human fingerprints on a poly(vinylidene difluoride) membrane (PVDF) by scanning electrochemical microscopy (SECM) has been developed. Compared to a classical ink fingerprint image, here the ink is replaced by an aqueous solution of bovine serum albumin (BSA). After placing the "inked" finger on a PVDF membrane, the latent image is stained by silver nitrate and the fingerprint is imaged electrochemically using potassium hexachloroiridate (III) (K_3IrCl_6) as a redox mediator. SECM images with an area of 5 mm × 3 mm have been recorded with a high-resolution using a 25-μm-diameter Pt disk-shaped microelectrode. Pores in the skin (40–120 μm in diameter) and relative locations of ridges were clearly observed. The factors relevant to the quality of fingerprint images are discussed.

Keywords: Scanning electrochemical microscopy; Silver staining; Fingerprint; Imaging

1. Introduction

Fingerprints, impressions of the friction ridges of all or any part of a human finger, have appeared at various stages of human history, for example on ancient potteries [1–3]. Fingerprinting has often been and is still considered as one of the most widely used biometric methods. It provides a valuable physical evidence of identification, as it is among the few biometric signatures that can be truly unique and invariable for an individual. There are, in general, three forms of fingerprint evidence that may be found at crime scenes: visible (or patent) fingerprints such as those made when an ink-coated finger touches a surface and leaves prints, impression (or plastic) fingerprints, which are a mechanical impression in soft materials such as wax, and latent fingerprints, which result from a transfer of secretions from the finger to a surface. In the past, powder dusting [4], ninhydrin spraying [5], iodine fuming [6], and silver nitrate soaking [7] were the four most commonly used techniques of latent fingerprint development. These conventional techniques are quite effective in the recovery of latent fingerprints under many ordinary circumstances. However, latent fingerprints can be deposited on objects or surfaces with unique characteristics: surfaces with multicolored backgrounds such as bank notes, surfaces contaminated with blood or other body fluids, and porous surfaces such as paper. Under these conditions, traditional methods of latent fingerprint development are often ineffective.

Scanning electrochemical microscopy (SECM) [8,9], a scanning probe technique, has been successfully developed into a powerful analytical tool for the kinetic measurements of heterogeneous and homogeneous reactions [10–13], for high-resolution imaging of biomolecules immobilized onto various surfaces and biological systems [14–26], and for microfabrication [27–29]. Instrumentally, SECM comprises a microelectrode as a tip, i.e. an electrode with a micro-disk diameter of 25 μm or smaller to electrochemically detect a specific redox species near the surface of a substrate, a high-precision position controller, and a bipotentiostat. In SECM experiments, the microelectrode is brought to the vicinity of the substrate surface, where the electrochemical response of the tip is recorded as a function of the lateral tip position (x, y) for imaging. Compared with other scanning probe microscopic techniques, SECM possesses some unique features. For example, it is

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capable of imaging chemical or biochemical activities present at a substrate surface and can image samples with relatively large surface areas (a few square centimeters). The latter feature makes SECM particularly advantageous over other scanning probe techniques for the imaging of latent fingerprints on a PVDF membrane. Moreover, SECM also has a well-developed quantitative theory.

We had previously shown that the SECM approach could be used to image silver or copper stained proteins [30,31]. These reports demonstrated the feasibility of using SECM for visualizing protein spots on a membrane surface. More recently, we improved this methodology as a highly sensitive tool of imaging proteins separated by gel electrophoresis, electroblotted on PVDF membranes and then silver stained [32]. Here, the technique is used to visualize latent fingerprints on a poly(vinylidene difluoride) (PVDF) membrane using SECM imaging of silver stained proteins. The fingerprints were formed on the membrane by microcontact printing (μCP) [33,34], using a human finger rather than a poly(dimethylsiloxane) stamp. An aqueous solution of bovine serum albumin (BSA) at 1 mg/mL concentration was used as the "ink". This methodology takes advantage of the high sensitivity of SECM towards the small variation of electrochemical properties at the substrate surface. It is also applicable to bloody latent fingerprints. The SECM images of the human fingerprints are of comparable or better quality than those obtained by conventional optical methods.

2. Experimental

2.1. Chemicals and materials

All chemicals were used as received. Methanol (Merck), sodium acetate anhydrous (>99%, Fluka), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, >99.5%, Fluka), sodium carbonate anhydrous (Na_2CO_3, >99.5%, Fluka), formaldehyde (37 wt% solution in water, Aldrich), silver nitrate ($AgNO_3$, >99.5%, Fluka), ammonium nitrate (NH_4NO_3, ⩾99.5%, Fluka), tungstosilicic acid hydrate (>99.9%, Aldrich), acetic acid (>99.8%, Fluka), potassium hexachloroiridate (III) (K_3IrCl_6, Aldrich), potassium nitrate (KNO_3, >99%, Fluka). Immun-Blot PVDF membranes for protein blotting (0.2 μm) were purchased from Bio-Rad (Hercules, CA, USA). Water was deionized to a conductivity of 18.2 μS cm^{-1} using a Milli Q plus 185 from Millipore. Bovine serum albumin (BSA, ⩾98%) was purchased from Sigma. Alumina 1 μm, (0.3 and 0.05 μm,) and Mastertex polishing cloths from Buehler were employed to polish the 25 μm-diameter disk shaped microelectrode.

2.2. Preparation of human fingerprints on the PVDF membrane

The fingerprints were formed by μCP of an "anonymous human finger" inked by a BSA solution on a PVDF membrane. The hydrophobicity of a PVDF membrane makes it an ideal support for binding proteins. Because of the hydrophobic nature of PVDF, it was first wetted in methanol for 1–3 s and then immersed in water for 1–2 min to elute the methanol when used as the substrate for fingerprints. (*Caution*! Once the membrane has been wetted with water, do not allow it to dry until the proteins have been transferred to it.) Prior to the μCP process, the finger of the anonymous volunteer was thoroughly cleaned with deionized water and dried with N_2. After "inking" the finger for 2 min with a 1 mg/mL BSA solution and allowing it to dry under a N_2 stream, it was then gently pressed onto the pre-wetted PVDF membrane substrate for 30 s. After removal of the finger, the protein marked membrane was submerged in a 1% sodium acetate solution for the subsequent silver staining process.

The optical fingerprint on the PVDF membrane obtained by inking the same finger using a standard writing ink was prepared in the same manner. After carefully cleaning the finger with deionized water and drying it with N_2, it was inked for 10 s, and then placed into conformal contact with a pre-wet PVDF membrane substrate for 10 s. After removing the finger, the fingerprint on the membrane substrate was imaged by an optical laser-scanner (HP Scanjet 4890).

2.3. Silver staining procedure of protein fingerprints on the PVDF membrane

The staining process followed for the procedure was that outlined by Sørensen et al. [35]. The protein fingerprinted sample was washed 15 min in 1% sodium acetate. It was then rinsed twice with water for 1 min. The sample was sensitized 15 min in 0.1% sodium thiosulfate, and it was then rinsed twice with deionized water for 1 min. After rinsing, the sample was submerged in a Gallyas staining solution made from two stock solutions (A and B), which can be stored for months at room temperature when protected against the light: (A) 5 g sodium carbonate dissolved in 100 mL of water; (B) 0.2 g ammonium nitrate, 0.2 g silver nitrate, 1 g tungstosilicic acid, and 0.5 mL 37% formaldehyde were added to 100 mL of water. The Gallyas stock A and stock B were mixed 1:1 under intensive shaking and the sample developed in this for 10 min. The development was stopped in 10% acetic acid for 5 min, and then the sample was dried for further characterization by SECM (CH Instruments Model CHI 900, USA).

2.4. SECM measurements

A three-electrode setup was employed with a 25-μm-diameter Pt disk shaped microelectrode as the amperometric SECM tip as schematically presented in Fig. 1. The counter and quasi-reference electrodes were a Pt wire and a silver wire, respectively. The protein fingerprinted membrane was fixed on a microscope glass slide. This cell assembly was secured onto a platform which includes three