

Supporting information

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Electrochromic enhancement of latent fingerprints by poly(3,4-ethylenedioxythiophene)

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EXPERIMENTAL PROCEDURES

Traditional visualization methods

For comparison purposes, fingerprints were also enhanced using three standard methods: dusting with (dry) powder, application of wet powder and cyanoacrylate (“superglue”) fuming. The dusting method used standard black powder (WA Products), applied with a mop head squirrel brush. Wet powder - a mixture of iron oxide and detergent (Codeco and distilled water) - was made to a consistency viscous enough to coat a surface but sufficiently optically transmitting that one could see the underlying surface through the resultant film. Wet powdered samples were developed by painting on the mixture in perpendicular directions to ensure particles attached to the deposited fingerprint ridges. Samples were then rinsed under slow running water to remove excess wet powder mixture and placed in a drying cabinet (60 °C) for 1 hour. Superglue treatment was carried out in a commercial superglue fuming cabinet (MVC 5000, Foster and Freeman, Evesham, UK) set to 78.9% humidity (achieved after ca. 8 minutes), followed by 15 minutes of fuming at 119.4 °C. Samples were then removed from the cabinet, dipped in a solution of Basic Yellow 40 dye (2 g l⁻¹ in aqueous 60% ethanol), rinsed under slow running water and left in a drying cabinet (60 °C) for 1 hour.

Sample “history” variation by pre-treatment

To simulate plausible object “histories” prior to location and visualization, the deposited fingerprints were subjected to a number of different pre-treatments before their enhancement with the polymer. The least challenging one (from an enhancement perspective) was simply being left in air (laboratory environment) for systematically varied periods of time, ranging from 1 hour to 28 days. Samples were also exposed to more extreme conditions, including heating in an oven (150 °C) or leaving under water (in each case for systematically varied intervals), washing in acetone and rubbing the prints off in hot (~40 °C), soapy water.

Fingerprint visualisation

Powdered samples (wet or dry reagents) were photographed using a Canon A480 digital camera which had a 1 cm super macro mode with auto focusing that allowed the fingerprints to be photographed with the camera only 1-3 cm away from the lens. Samples that had been superglued and dyed with BY40 required fluorescent lighting (4x4 Crime Lite: blue, 430 – 470 nm) in order to be photographed. The samples were photographed using a Fuji Fine Pix S2 Pro camera equipped with a Nikkor lens (55 mm) and filter (476 nm). Digital image enhancement software (GNU Image Manipulation Program 2.6.7, GIMP) was used to crop the images to the relevant area and increase contrast by adjusting colour levels.

Magnified optical images were acquired with a Meiji Techno MT7100 trinocular microscope operated by uEye (IDS GmbH).

FINGERPRINT QUALITY EVALUATION

Grade	Description
0	No development
1	No continuous ridges; all discontinuous or dotty
2	One third of the mark comprised of continuous ridges; remainder either show no development or dotty
3	Two thirds of the mark comprised of continuous ridges; remainder either show no development or dotty
4	Full development; whole mark comprised of continuous ridges

Table S1: Bandey fingerprint grading scheme¹.

The quality of each fingerprint, both “as found” and subsequent to the various enhancement treatments, was evaluated using the Bandey scale. This five point scale (see Table S1), developed by the UK Home Office, is a widely used means of evaluating the quality of fingerprint images in a research context. While not used in legal proceedings, the generally accepted view is that a grade 3 or a grade 4 image would permit unambiguous identification of an individual; lower grade images would not be considered as being of evidential value.

PEDOT FILM CHARACTERIZATION

Evaluation of film thickness

The amount of polymer deposited on the surface was determined by coulometric assay. A criterion for this to be valid is full electroactivity, i.e. the film must undergo complete redox conversion on the timescale of the measurement. In the context of a cyclic voltammetric experiment, the diagnostic for this may be expressed in two (equivalent) ways: either the charge passed must be independent of potential scan rate ($v / \text{V s}^{-1}$) or the peak current must increase linearly with potential scan rate. If the peak current increases less than linearly (most commonly in a square root fashion, characteristic of diffusional control), the charge decreases with scan rate, signalling progressively diminishing partial redox conversion as the experimental timescale is decreased. A representative plot of peak current *vs* scan rate is shown in [Fig. S1](#). The linearity unambiguously indicates complete redox conversion of the film in each half cycle.

Integration of the current (at any selected scan rate) gives the charge, Q / C . The spatial distribution of the polymer across the surface is non-uniform – this is the basis of the fingerprint image – but one may consider a laterally averaged coverage (as is typically done for notionally “uniform” but in practice rough films), $\Gamma_{av} = Q/nFA$, where n is the doping level (here we use the accepted value for PEDOT, $n = 0.33$). The spatially averaged film thickness is then given by $h_{f,av}^0 = \Gamma V$, where V is the molar volume of EDOT monomer. From the perspective of the true thickness, h_f , at a location (between fingerprint deposition ridges) where PEDOT deposition has occurred, the value of $h_{f,av}^0$ is an underestimate in two respects: the implicit lateral averaging associated with the coulometric assay (indicated by the subscript “*av*”) and the extent to which equating the actual concentration of EDOT monomer sites ignores solvent swelling (indicated by the zero superscript, to signal no solvation).

[Figure S1 here]

Fig. S1. Variation with potential scan rate of cathodic peak current for a representative PEDOT film used to enhance a sebaceous fingerprint. The fingerprint was deposited on stainless steel and left (under ambient conditions) for a period of 11 days before enhancement by PEDOT deposition. See main text for deposition procedure; deposition time: 250 s. Line shown is least squares fit to the data.

The molar volume of EDOT, $V = 106.8 \text{ cm}^3 \text{ mol}^{-1}$, corresponding to a concentration of EDOT monomer units in an (hypothetical) unsolvated film, $c^0 = 9.36 \times 10^{-3} \text{ mol cm}^{-3}$. For the PEDOT film represented by [Fig. S1](#), $Q = 28 \text{ mC}$ (over a total area, $A = 6.25 \text{ cm}^2$), from which the total coverage and spatially averaged polymer film thickness, respectively, are $\Gamma_{\text{av}} = 165 \text{ nmol cm}^{-2}$ and $h_{f,\text{av}}^0 = 177 \text{ nm}$. Reasonable estimates of the fraction of the surface available for polymer deposition (a factor of ca. 2, by visual inspection of the film) and of the solvent content (up to 50 v/o) indicate that the true local value of PEDOT film thickness in film-coated regions is $h_f \sim 700 \text{ nm}$.

Practical implementation

[Fig. S2](#) shows a set of images for a similar experiment to that represented by [Fig. 1](#) (main text), except that the initial latent fingermark was of lesser quality such that, despite clear enhancement by the PEDOT treatment, none of the combination of control parameters (potential and solution composition) generated an image that showed high quality detail throughout.

[Figure S2 here]

[Figure S2](#). Effects of ambient medium and applied potential on a single sebaceous fingerprint image subjected to enhancement by PEDOT deposition and viewing under various conditions. Fingerprint, deposited on stainless steel, then stored for 3 days in ambient laboratory conditions prior to the observations

shown. Panel *a-e* following PEDOT deposition (see main text; deposition time 150 s). Sample environment: panel *a*: *ex situ*; panels *b* and *c*: *in situ* exposed to 1 mol dm⁻³ H₂SO₄; panels *d* and *e*: *in situ* exposed to 1 mol dm⁻³ H₂SO₄ / 0.01 mol dm⁻³ SDS. Applied potential: panels *b* and *d*: 0.80 V; panels *c* and *e*: -0.80 V. Panel *f*: optimised whole fingerprint image created by assemblage of selected high contrast regions from the images of panels *a-e*.

It is clear that none of the individual images provides ideal contrast across the entire fingerprint. However, it is equally clear that imposition of different conditions of potential and electrolyte composition, generating different degrees of optical density and contrast (which may be regarded as “sensitivity” and “selectivity”, respectively), allow optimal viewing of selected regions. One may therefore consider assembling a complete image of high contrast by taking selected optimally contrasted sub-areas of the whole fingerprint.

The outcome of this approach is shown in panel *f* of [Fig. S2](#). Note how, for example, trench overfilling (dark, low contrast region) in the lower left of panel *c* is replaced by the optimally contrasting (optically lightening) the same region under the conditions of panel *e*. Similarly, the poorly contrasting (pale) region in the top right of panel *b* is replaced by the optically darker image of this region under the conditions of panel *c*. Since the images are of the same fingerprint (same PEDOT film, merely subjected to different potential and solution control parameters) and provide adequate continuity of ridge detail, there is no loss of whole fingerprint fidelity in the assemblage process. This procedure underscores the power of being able to reversibly adjust electroactive film properties by control from the “dry” and/or “wet” sides of the film.

References

1. H. L. Bandey, *Fingerprint development and imaging newsletter: the powders process, study 1*. Sandridge, UK: Police Scientific Development Branch, Home Office, 2004; Report No.:54/04.