



Latent fingerprint enhancement via conducting electrochromic copolymer films of pyrrole and 3,4-ethylenedioxythiophene on stainless steel



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ABSTRACT

Latent fingerprints, by definition, require chemical or physical treatment to render them visible. The broadly insulating characteristics of sebaceous fingerprint residue make the deposit act as a “mask”, directing electrochemical processes to regions of bare metal between the residue. We use this effect during electrooxidation of pyrrole (Py) and 3,4-ethylenedioxythiophene (EDOT) to form copolymer films on stainless steel: the outcome is a negative image of the fingerprint. The lower oxidation potential of pyrrole means that the copolymer is enriched in this component; quantitation using XPS shows that this is more pronounced for films deposited potentiodynamically than potentiostatically. Nonetheless, the accessible ranges of solution composition and deposition potential permit controlled deposition of films in which either (or neither) component is dominant. The films are electrochromic in a manner that depends not only on applied potential post-deposition (as expected), but also on deposition potential; this allows visible contrast optimization against the substrate. Poly(Py-co-EDOT) films permit observation of latent fingerprints on stainless steel with high definition of second level details used for identification purposes and, on occasions, finer (third level) detail. Imaging may be accomplished visibly (by film colour), compositionally (by mapping functional groups using vibrational spectroscopy) and topographically (using a 3D microscope).

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1. INTRODUCTION

The use of fingerprint images on a scientific basis for biometric identification dates back to the mid nineteenth century [1]. In recent decades other approaches have been developed, notably based on DNA sequencing, but the ease of collection of fingerprint evidence, its robustness to contamination issues (commonly the basis of challenges to DNA replication methods) and public acceptance of the concept of fingerprint uniqueness have maintained the prevalence of fingerprint evidence in the identification of individuals for forensic and other purposes. As detailed below, most fingerprint evidence requires some form of treatment to render the mark sufficiently visible for analysis and numerous physical and chemical methods have been devised for visualizing fingerprints on diverse surfaces [1]. Despite significant effort being put into their optimization, the success rate in obtaining fingerprint images whose clarity and fidelity permit unequivocal identification remains surprisingly low – in the case

of metallic surfaces, the recovery rate is well below 10 percent [2–4]. Rather than pursue the evolution of methods that attempt to make the *fingerprint residue* itself visible, we have adopted the complementary approach of using electrochemically driven processes to deposit a visible material on the regions of *bare metal* between the fingerprint residue [5,6]. We have previously demonstrated the concept via electrodeposition of polyaniline [5] and poly(3,4-ethylenedioxythiophene) (PEDOT) [6] films, whose electrochromic properties introduce an additional level of sophistication in the optimization of visual contrast between the reagent and the surface. Here we extend this concept to copolymer films, whose compositional variation provides greater opportunities to optimize visual contrast with the surface.

Friction ridges on the hands – and particularly the fingertips – have evolved to enhance the sense of touch and to assist with effective gripping of objects. Since the detailed pattern of these ridges has been found to be unique to an individual [1], it may be used as a means of identification. Although the uniqueness was proved only relatively recently, exploitation of the concept of variation in fingerprint ridge patterns has been used as a “signature” since ancient times [1]. Furthermore, the invariance of the pattern during life (except as a result of major injury to the

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fingers) means that fingermarks whose deposition is separated in time can still form the basis of an identification. In fact, since the pattern can persist for some time after death [7], it may also be used for identification of deceased individuals, for example as a result of a violent crime, an accident or a natural disaster.

In the case of criminal investigations, the image involved is generally as a result of the transfer of material to and/or from a surface that is touched by the finger. This is commonly expressed in terms of Locard's principle [8,9] that "every contact leaves a trace". Specifically, a small amount of the substance(s) on the surface of the ridges on the finger is transferred to the touched object, much as would occur in the use of an inked rubber stamp. If the substance involved has a contrasting colour to the surface, as in the case of blood or paint transferred onto a light coloured plastic surface, then this would be referred to as a *visible fingerprint*. Alternatively, if there is no contrast in colour or the transferred substance is colourless, then this is referred to as a *latent fingerprint*. The latter situation is the most common source of forensic evidence, since its lack of visibility frequently means that a criminal – probably with limited available time – is less likely to remove the fingerprint.

Even in the absence of external substances, fingermarks are inevitably left on a surface as a result of secretions from eccrine glands located on the fingers or via contact of the fingertips with the facial region, where sebaceous glands are found. Eccrine sweat is broadly aqueous and has a high inorganic salt content [1]; indeed, there is sufficient sodium chloride to corrode metal surfaces, a fact that has been exploited for fingerprint visualization on brass [10]. There are also significant levels of lipids and amino acids, whose reaction with reagents such as ninhydrin can be used to reveal latent fingerprints on certain surfaces, such as paper [1]. Sebaceous sweat is broadly organic-based and contains a complex mixture of fatty acids, phospholipids, wax esters, sterols and squalene; this mixture, whose composition varies between individuals, is generally referred to as *sebum* [1,8]. The common feature between eccrine and sebaceous fingermarks is that they are colourless: such *latent* fingerprints, by definition, require physical or chemical treatment to reveal the image.

The simplest traditional protocol for latent fingerprint visualization involves dusting with a powder: this may be fluorescent [11–13], magnetic [1,14,15] or thermoplastic in nature and the interaction with the residue is essentially physical adherence. Chemically-based protocols generally target one of the components of the sweat residue, according to the type of deposit transferred to the surface. Common approaches include use of ninhydrin solution (delivered by dipping or spraying) [1], vacuum metal deposition [16], small particle reagent [17], and fuming with cyanoacrylate [21], and fuming with cyanoacrylate [18,19] (colloquially, "superglue"). In some instances, a second stage is required to complete the visualization, e.g. the white polymer produced from cyanoacrylate is visualized by exposure to solutions of fluorescent dyes (Basic Yellow 40, Rhodamine 6G, Safranin O and Basic Red 14), although new cyanoacrylate reagents pre-functionalized with a fluorophore have recently been introduced [20,21]. Fluorescent inorganic materials, such as cadmium sulphide nanocomposites that interact with fatty acids and amino acids, are also used [22]. Novel physically-based approaches to visualizing a fingerprint image include mapping of surface work function (using a Scanning Kelvin Probe) to provide an image based on its spatial variation [23,24] and electrostatically induced attachment of carbon particulates to semiconducting oxides on brass surfaces (e.g. bullet casings) in a pattern that reflects the fingerprint [10].

The pattern of a fingerprint, whether intrinsically visible or latent and visualized by any of the above treatments, can be described at three levels of detail [1,8]. So-called first level detail

describes the general type of the fingerprint pattern as a whole: the pattern type may be a loop, a whorl or an arch. Clearly, this is insufficient for unique identification, but it can permit elimination. So-called second level detail corresponds to characteristic *minutiae* within the fingerprint. Such features include a *ridge ending*, a *bifurcation*, a *lake* (where two split ridges rejoin after a bifurcation), a *dot*, an *island* (a short independent ridge), a *spur* and a *crossover* (between two parallel ridges). The presence of – and particularly the spatial relationship between – second level detail features is the basis of fingerprint identification, so the facility to image these with high fidelity is vital. So-called third level detail involves a number of smaller features, notably pores along the ridges. These are often not resolved and are not currently used for identification in practice, but the facility to image these reliably is of interest since they might be useful in cases where image detail is sparse, for example partial fingerprints.

We recently demonstrated the concept of a complementary approach to conventional methods. The method is based on the simplistic notion that the fingerprint residue is electrically insulating. While there may be salts and other species within the residue that impart some conductivity, the practical outcome is that there is sufficient resistance locally to prevent electron transfer between the substrate metal and solution species. Thus, we have electropolymerized aromatic monomers (aniline and EDOT) on the bare metal at the base of the "trenches" formed by the fingerprint residue [5,6]. Essentially, the insulating fingerprint residue is used as a template (or mask) through which the reagent is deposited, to generate a negative image of the fingerprint. The basis of this approach was demonstrated by Bersellini et al. [25], who deposited polypyrrole electrochemically on fingerprinted metal surfaces. The limited distance over which electron transfer can occur means that very small amounts of fingerprint residue can be used to generate a clear image. Operationally, this offers the promise of retrieving usable images from fingerprints on objects subject to environmental degradation or ageing [26].

The electrochromic properties of films based on polypyrrole (PPy) [27], polyaniline (PAni) [28] and poly(3,4-ethylenedioxythiophene) (PEDOT) [29–37] homopolymers have been extensively studied. Composites [38], bilayers [39] and copolymers [40,41] amongst these families of materials have also been explored. Polypyrrole and polyaniline are multi-chromic: PPy is blue-violet in the p-doped state and yellow/green in the undoped state, while oxidation of leucoemeraldine (the fully reduced form of PAni) yields emeraldine (green or blue, according to protonation state) and then pernigraniline (blue/violet) forms. Against these attractive attributes, PPy has limited chemical stability and is irreversibly oxidized (commonly referred to as "over-oxidation") to an electroinactive form at modest positive potentials [42]. PAni has good stability to redox cycling, but again only within a restricted potential range [43], and its electroactivity (upon which the electrochromic enhancement method is reliant) is pH dependent. Conversely, PEDOT has excellent stability, but the optical variation is less pronounced: light blue in the undoped form and dark blue in the p-doped form. Although the narrow band gap of PEDOT means that its n-doped form is in principle accessible [44], the practical requirement to operate in aqueous media precludes exploitation of this opportunity; similar issues arise with polypyrrole [45].

Collectively, PPy, PAni and PEDOT possess the desired attributes, but each of these homopolymers possesses a characteristic that limits its applicability in this context. The concept we explore here is the possibility that copolymers might permit combination of the positive attributes of the homopolymers in a manner that has can be exploited for the visualization of latent fingerprints. The strategy we pursue is based on formation of copolymers of pyrrole and EDOT.

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