Electron Transfer Reactions for Latent Fingerprint Visualization: From Nanoscale Control of the Fundamentals to Macroscopic Imaging

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Fingerprints are unique time-invariant attributes of an individual. Consequently, they are the most frequent physical evidence used to identify a suspect in a criminal investigation or the victim of a crime or natural disaster. An image of the fingerprint (a fingermark) left on a surface by the transfer of material between the fingertip and the surface can establish contact between the individual and either an object (a weapon or a valuable item) or a fixed location (the crime scene). While some marks are immediately visible (e.g. a mark made by transfer of blood from the fingertip to the surface), these may be removed – colloquially "wiped" – by the criminal. Thus, in practice most marks are so-called *latent* (non-visible) fingermarks that require chemical treatment to generate a visible image. Despite the impressive range of chemical treatments available, practical issues associated with ageing of the mark or environmental exposure of the substrate object significantly limit the success rate of visualizing a latent fingermark. Thus, there is significant scope for novel chemical treatments offering enhanced selectivity and sensitivity. This presentation describes the contribution of electron transfer reactions (redox processes) to this endeavor and reveals the wide variety of reaction type, reagent materials, and substrate surfaces that may be involved.

Viewed as a whole (so-called first level detail), fingerprints can be classified into loops, arches and whorls; this level of detail may permit elimination of an individual but clearly cannot lead to an identification. The lateral (horizontal) patterning of so-called second level features (such as ridge endings, crossovers and bifurcations) form the basis of identification. Finer (third level) details, including pores and detailed ridge shape, are recognized but the challenge of imaging these means that in practice they are seldom utilized.

Superficially, the distance scale is *macroscopic*: a typical fingermark ridge width is ca. 100 μm. However, the aspiration of a high quality image involves resolution of third level detail at the *mesoscopic* level: ridge edge shape capture requires resolution of ca. 1 μm. Successful fingermark visualization requires the facility to deliver the reagent with high spatial selectivity to *either* the deposited residue (representing ridges on the finger) *or* the bare substrate (representing furrows on the finger), such that there is visual contrast between the ridge and furrow areas. However, the *lateral* image quality indicated above requires *vertical* control of reagent deposition at the *nanoscale*. Here we explore how latent fingermark visualization can be accomplished by electrochemically-based molecular mechanisms involving metallic and polymeric materials.

Two established, but previously poorly mechanistically understood, metal deposition processes are physical developer (PD) and multi-metal deposition (MMD). PD involves redox generation of silver nanoparticles that deposit selectively on fingermark residue on paper substrates, such as documents, correspondence and paper currency. We show how mechanistic understanding of a recent PD re-formulation has been used to overcome the environmental outlawing of a critical surfactant in the classical PD process. This next generation formulation is capable of revealing latent marks up to a century after deposition.

MMD is a more sophisticated variant, in which gold nanoparticles pre-deposited on the residue act as nucleation sites for silver deposition. These can reveal marks on thin plastic films, typical of those used to wrap drugs and explosives. By determining the dynamics of redox-driven silver deposition on ridge *vs* furrow regions of the mark, we are able to place a numerical value on image contrast.

For reactive metal surfaces, typified by copper (and its alloys) and mild steel, we adopt a complementary strategy in two respects: the electron transfer process takes place at the solid/solution interface. The redox-generated metal is deposited on the substrate rather than the fingermark residue. This strategy exploits the fingerprint residue as a template ("mask") to direct electrochemically generated reagent to the *bare surface* between the deposited ridges, creating a negative image of the fingerprint. When the surface is a reactive metal (Cu or Fe), a more noble metal (Ag) can oxidize exposed substrate atoms. The electron transfer process results in solution oxidant (here, Ag ions) being reduced to elemental metal that deposits on the surface and dissolution of an equivalent amount of substrate. We show how complexing agents may influence both reaction thermodynamics and kinetics. Optical and SEM imaging and EDAX surface analysis reveal high quality images with clear third level detail.

When the surface is an inert metal, the above galvanic exchange cannot take place. This is exemplified by exemplified by stainless steel, a surface of forensic relevance to knife crime. In this instance, electrochemically driven oxidation of aromatic monomers at regions of bare metal results in deposition of polymer to create negative images of latent marks. This can be accomplished *via* polyaniline, PEDOT or poly(pyrrole-co-EDOT) films. We show how variation of applied potential to these electrochromic systems offers the prospect of optimization of visual contrast in terms of light *absorption*. More recently, we have explored the prospect of light *emission* by incorporating fluorescent dyes (Methyl Red, Methyl Orange, Indigo Carmine, Basic Yellow 40) in the polymer films using functionalization, ion-exchange and physical encapsulation strategies.

Having demonstrated the potential of these electrochemical latent fingermark visualization strategies, we discuss aspects of technology transfer to the forensic practitioner environment. Technically, this includes practical (non-ideal) object and surface scenarios, integration into sequential treatment regimes, and the use of software to both enhance and interpret the images. Operationally, this involves procedural validation and adherence to appropriate standards. Positive outcomes rely on collaborative expertise provided by practitioners, researchers, regulatory authorities and investigators. We discuss how this can be realized through engagement of these parties and researcher use of the image capture and enhancement technologies used by practitioners.