Metal-containing Nanoparticles and Nano-structured Particles in Fingermark Detection

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Abstract

This article reviews the application of metal-containing nanoparticles and nano-structured particles to fingermark detection. This area of research is attracting significant interest as advances in nanoscience are being incorporated into the field of forensic fingermark detection. Although more research is needed before some of the techniques presented can be implemented in routine casework, nanotechnology is likely to play a major role in the future to deliver more selective and more sensitive ways to detect and enhance fingermarks.

Keywords. fingermarks, fingerprints, nanoparticles, luminescence, nanotechnology.

Contents

1. Introduction

1.1. Fingermarks

Fingermarks are one of the most useful forms of physical evidence in identification and generalized proof of identity, despite of the recent growth in the use of DNA. The ridge patterns are characteristic to each person and immutable as they are formed deep in the skin, universal, and leave marks on objects handled with bare hands [1].

In general there are three categories of fingermark evidence that may be found at a crime scene. Visible marks can be formed by contact contaminated with blood, paint, oil, grease, etc. (positive image) or when material such as dust is removed from the surface by contact (negative image). Visible fingermarks are generally straightforward to detect. Indented or plastic marks can be produced through contact with soft surfaces such as putty, candle wax, or wet paint. Latent marks, which are present but invisible, are the most common form of fingerprint evidence and the most problematic. The application of optical, physical, or chemical techniques are required to visualize latent fingermarks [1]. The choice of the technique for fingerprint development is dependent on the composition of latent fingermarks, on the type of substrate and on the ability of the technique to be applied in sequence in the context of the case.

The fingermark is a complex mixture of natural secretions of the body (mostly sweat from different type of glands) and contaminations from the environment [1]. Secretions from three types of glands, eccrine, apocrine, and sebaceous, may be present in latent fingermarks (see Table 1). The constituents of the deposit are mostly water (99%) and minor amounts (up to 1%) of inorganic and organic compounds. Sebaceous glands are associated with hair roots and located on throughout the body, except on the palms, or soles of the feet. Glycerides, fatty acids and wax esters are found in the sweat from sebaceous glands.

Table 1. Main Chemical Constituents of the Glandular Secretions [1].

Source	Constituents	
	Inorganic	**Organic**
Eccrine glands	Chlorides Metal ions (Na^+, K^+, $Ca2^+$) Sulfates Phosphates Amonia Water (>98%)	Amino acids Proteins Urea Uric acid Lactic acid Sugars Creatinine Choline
Apocrine glands	Iron Water (>98%)	Proteins Carbohydrates Sterols
Sebaceous glands		Glycerides (30-40%) Fatty acid (15-25%) Wax esters (20-25%) Squalene (10-12%) Sterol esters (2-3%) Sterols(1-3%)

The amount and constituent of individual secretions are variable and individual glandular secretions also vary. Environmental conditions such as temperature and humidity, exercise, stress etc affect the rate of production of eccrine sweat. Its composition also varies in relation to

age, sex, medical condition and diet. Eventually these factors influence the quality of developed fingermarks, along with environmental conditions post-deposition.

1.2. Detection of fingermarks

A variety of techniques have been used to enhance the visibility of latent fingermarks. The combination of optical methods (absorption, diffuse reflection, luminescence, UV absorption and reflection) [1-5], physical methods (powdering, small particle reagents, vacuum metal deposition) [4, 6-10], physical/chemical methods (physical developer, multi-metal deposition, iodine, cyanoacrylate) [4, 11, 12] and chemical methods (ninhydrin and its analogues, metal complexation after ninhydrin treatment, DFO, 1,2-indanedione, and genipin) [4, 13-21] allows for the development of fingermarks deposited on various surfaces.

1.3. Nanoparticles and nano-structured particles

Nanotechnology involves the creation of functional materials, devices and systems using matter with dimensions on the nanometer length scale (1-100 nanometers), and the exploitation of properties unique to the nanoscale. One advantage of nanotechnology is the often vastly increased ratio of surface area to volume present in many nanomaterials compared to the bulk material. This provides new possibilities in surface-based science including forensic fingermark detection. A number of other physical phenomena become noticeably more pronounced as the size of the system decrease. These include, for example, the crystal phase of the material, its doping properties and interactions with light, and electron transport properties [22].

Nanoparticles are much smaller than most of the particles currently used in fingerprint detection, which are in the order of 1-10 μm in size [23]. Nanoparticles are distinct, non-aggregated particles with nanometre-size diameters, and nanostructured particles often exist as aggregates of nanosized particles, which may be up to microns in diameter. Because of the increasing interest in their use in fingermark detection, we emphasise the difference between

nanoparticles and nanostructured particles, which can have quite different properties such as surface area and roughness that in turn lead to different chemical and physical properties.

2. Metal Particles

In this section we describe nanoparticles that have been used for fingermark detection that contain metals in their elemental state. The most common of these are gold nanoparticles, due in part to the stability of gold towards oxidation. Nanoparticles containing metallic silver are also reasonably stable however only one example of these has been reported in the context of fingermark detection. The topic of physical developer (where a thin coating of metallic silver is deposited from a silver salt solution) is not addressed in detail in this report, the reader is directed to reference [24] for further discussion.

2.1. Multi-metal deposition

Multi-metal deposition (MMD) is a two-step wet chemical process for the detection of latent fingerprints combining the principles of small particle reagent (SPR) and of a physical developer. The first step involves immersing the item in an aqueous gold nanoparticle solution of pH 2.5-2.8 (the solution pH is critical in this technique, see below). Generally, fingermarks show poor contrast after this step. In the second step of the procedure, the item is treated with physical developer to enhance the fingermark contrast. This results in fingermark ridges stained from light grey to black [1, 4, 25].

It has been proposed that under acidic conditions (low pH), proteins or amino acid-containing components within a fingermark are protonated and thus carry a positive charge. Negatively charged gold nanoparticles (negative due to the absorption of stabilising citrate anions) are deposited preferentially on the fingermark ridges through electrostatic interactions [26, 27]. In addition, the gold nanoparticle surfaces are hydrophobic [28] while many protein surfaces are also hydrophobic [29]. Hence the binding of the gold nanoparticles with proteins may be facilitated by both electrostatic and hydrophobic interactions [25, 28]. It may be expected [25] that electrostatic interactions dominate at low pH. Choi *et al* [30] used scanning electron microscopy to show that gold nanoparticles suspended in an aqueous solution at pH 2.65 and

containing 0.1% Tween 20 (surfactant), bind preferentially to latent fingermark ridges on nonporous surfaces such as glass, plastic and silicon wafer (see Figure 1). Changing the pH influences the binding to ridges but leaves valley regions unaffected. A comparison between SEM images of the fingermark ridge area of samples developed at pH 2.65 and samples developed with no pH adjustment (~ pH 6) shows significantly more particles are deposited on the fingermark ridge region of samples at pH 2.65.

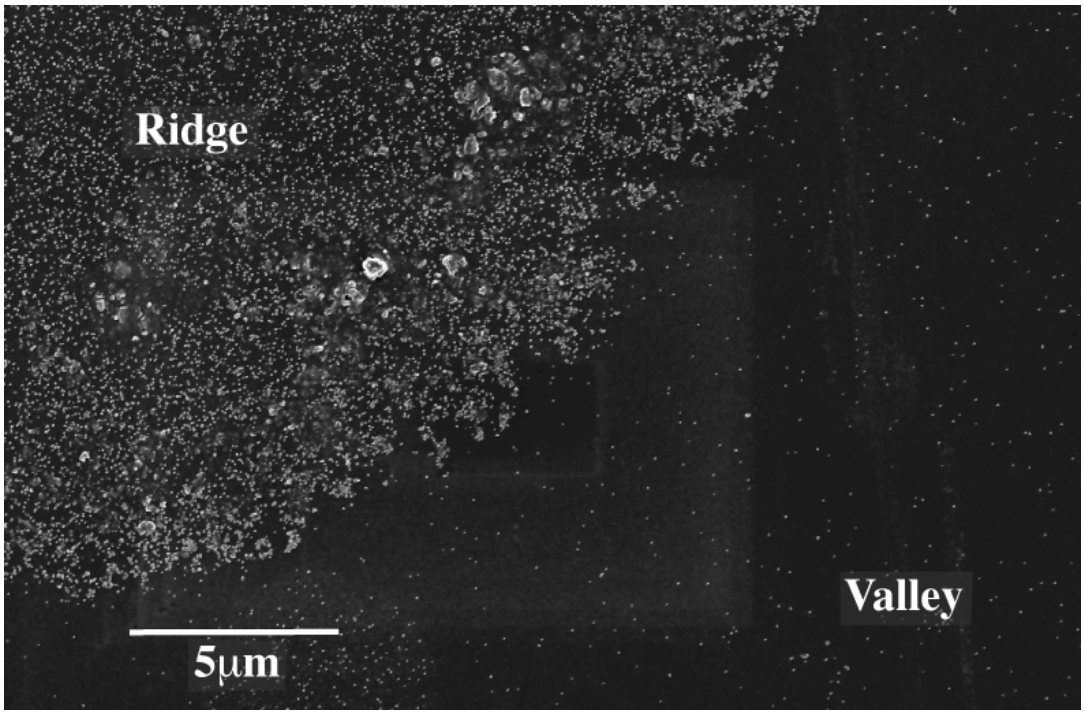

Figure 1. SEM image of the ridge-to-valley boundary region of a fingermark treated with gold nanoparticle solution at pH 2.65, with 0.1% Tween 20 surfactant. Bright dots are individual gold nanoparticles [30].

Once bound to the fingermark ridges, the gold particles serve as nucleation sites for the growth of silver particles from the physical developer treatment which acts as an amplification step [1, 26, 31]. The physical developer solution contains silver (Ag^{+}) ions, and in the presence of a reducing agent the ions are reduced to silver metal (Ag^{0}) on gold nucleating sites [7].

Consequently, contrast between the fingermarks and the background is significantly enhanced compared to the gold deposition step.

MMD was introduced by Saunders [32] in 1989 for visualizing latent fingermarks on a range of surfaces including porous and nonporous surfaces, wet surfaces, coloured and non-coloured surfaces, on adhesive tapes, and metal surfaces [33]. The procedure was subsequently investigated by Irrausch [34] and Allman *et al* [26]. Irrausch reported MMD is effective on plastic, glass, white paper, adhesive tape and expanded polystyrene. In addition, MMD is superior to conventional physical developer on certain papers. However, on dry surfaces, MMD is less sensitive than DFO or cyanoacrylate fuming. Allman and co-workers found MMD to be at least equal and often superior to cyanoacrylate fuming and VMD (vacuum metal deposition) on plastics/polythenes. Moreover, MMD shows promise in developing fingerprint marks on non-porous surfaces which had previously had proved difficult (for example, masking tape, beer bottle labels, and plastic gloves, cling film). Fingermarks in blood may also be enhanced by MMD [1, 4, 25]. It has been reported that latent fingerprints previously developed on the front side of photographic paper with cyanoacrylate were enhanced by MMD. Fingermarks were also developed on the back of the photograph, which had been previously processed with Ninhydrin [35].

Schnetz and Margot [12] modified MMD, yielding superior results by using smaller gold particles, an alternative physical developer, and accurate pH control (the MMDII method). An evaluation of MMD methods by Jones *et al* [25] found that MMD II produces superior results compared with the original MMD formulation in terms of sensitivity and selectivity and it is effective on a number of problematic semi-porous surfaces. In addition MMD can be successfully used in sequence after CAF and luminescent staining.

Becue *et al* [36] proposed a new MMD technique using gold nanoparticles modified with a cyclodextrin molecular host. Their procedure reduced the number of baths required (see Figure

2). The gold nanoparticles were functionalized by thiolated cyclodextrin, which could trap a dye the cavities. Satisfactory results were obtained on three different surfaces without further enhancement by physical developer.

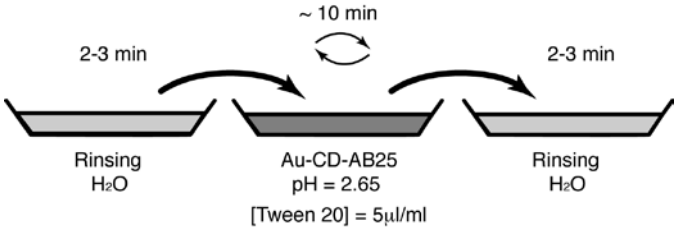

Figure 2. Experimental procedure of the MMD method of Becue *et al.* [36]

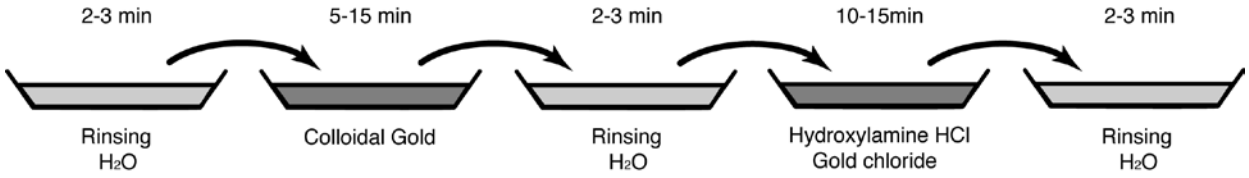

Figure 3. Experimental procedure of the SMD technique [37]

Recently, a single-metal deposition (SMD) technique was proposed by Stauffer *et al* [37]. SMD replaces the silver developer step with a gold enhancement procedure. The hydroquinone and hydroquinone/silver acetate baths used in the MMD procedure were replaced with one single hydroxylamine/gold chloride bath. Gold chloride provides gold(III) ions and hydroxylamine is the reducing reagent (Figure 3). Gold colloids deposited on fingermarks serve as catalysts to the precipitation of metallic gold (Au^0) from the hydroxyamine/gold chloride solution, thus increasing the size of the gold colloids. This principle is based on an electroless deposition reaction, the same principle behind silver precipitation. The results obtained by SMD in fingerprint development offer similar results to those obtained using MMD in terms of sensitivity and selectivity.

Sametband *et al* [38] described the application of gold nanoparticles using lipophilic interactions between fatty acids of fingermarks to develop latent marks. Gold nanoparticles stabilized with alkanethiols (octadecanethiol, tetradecanethiol, and decanethiol) were prepared according to the existing literature [39]. They found a relationship between the chain length of thiol and the developed fingermark quality with longer alkanes yielding clearer fingermarks.

Leggett *et al* [40] showed the possibility of detecting specific drugs or drug metabolites and simultaneously identifying an individual. Using gold nanoparticles functionalized with anti-cotinine, an antibody of cotinine (a metabolite of nicotine), fingermarks could be developed and it could be determined if the individual was a smoker. In their procedure, the anti-cotinine-nanoparticle conjugates were pipetted onto fingermarks and incubated. A fluorescent agent was then introduced and incubated and the fingermarks imaged. High quality fingerprint images were obtained (Figure 4). They repeated the procedure using anti-cotinine antibodies not attached to the gold nanoparticles to determine whether the nanoparticles were necessary. The presence of cotinine was confirmed but only poor quality fingerprints were obtained. Fingermarks from non-smokers were also developed but the lack of fluorescence indicated that cotinine was not present and the individual was not a smoker.

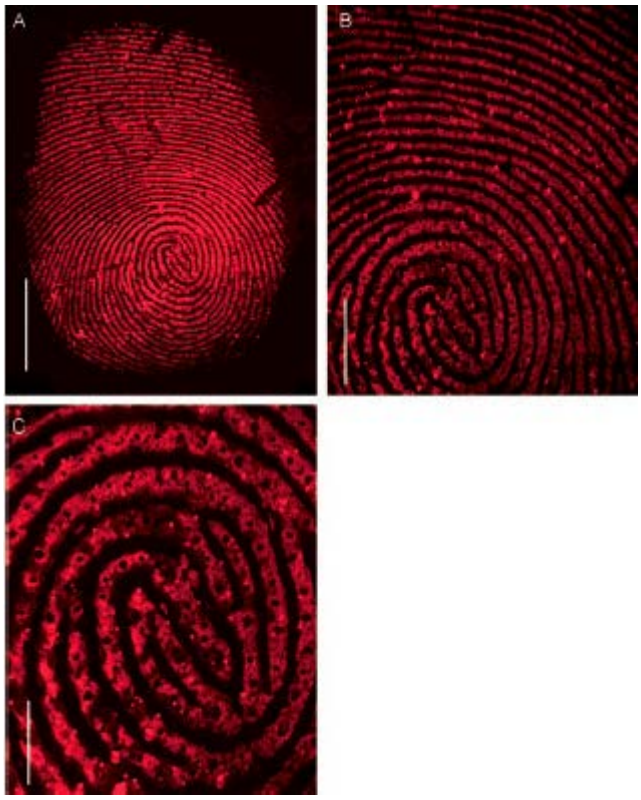

Figure 4. Fluorescence images showing detailed fingerprint information using antibody-functionalized nanoparticles. The images are taken from the thumb of a male smoker after 40 min sweating and illuminated using an Alexa Fluor 546-tagged secondary antibody fragment. Scale bar: 5mm (A), 2mm (B), and 1mm (C). [40].

Zhang et al. [41] recently showed that fingermarks developed using the MMD technique could be imaged using scanning electrochemical microscopy (SECM) where the silver layer is re-oxidised by the probe and $IrCl_6^{3-}$ acts as a redox mediator. The images, generated by amperometric feedback as the sample is scanned by the probe, show excellent detail (Figure 5). The authors posit that this technique can generate high-contrast images on patterned or textured surfaces where conventional imaging of treated marks is ineffective. However, before such an imaging technique could be readily applied on items submitted for examination in routine cases, the technology would need to improve so that larger areas can be scanned within a much shorter period of time.

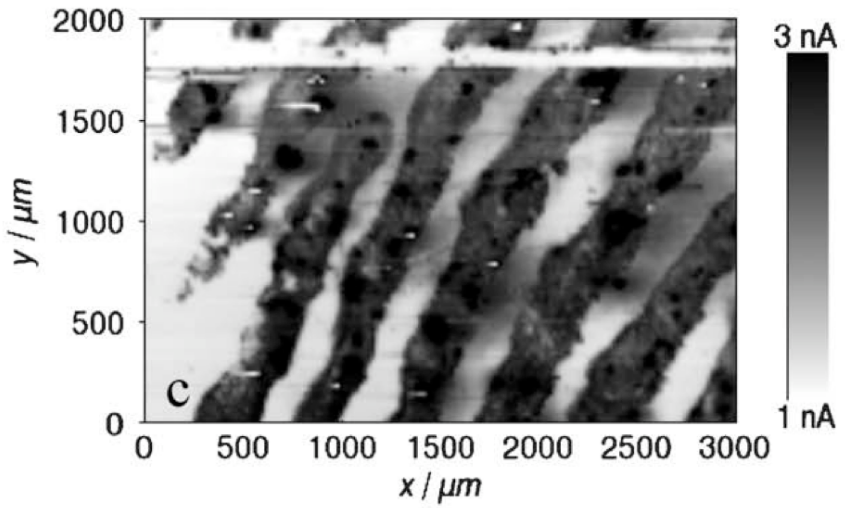

Figure 5. High-resolution SECM image of a fingermark developed by MMD. From [41].

2.2. Metal nanoparticles as powders

Fingerprint powdering remains the most commonly-used technique for the detection of fingerprints on non-porous surfaces at the scene. Powdering is relatively simple and inexpensive, and often satisfactory results may be achieved with a modest amount of training [1, 4]. The technique relies on powder adhering to moisture and oily components in fingermark ridge deposits. The effectiveness with which the powder adheres to the ridges depends on the size and shape of the particles; small, fine particles generally adhere more easily than large, coarse ones [10].

Choi *et al* [42] reported that gold and silver nanoparticles could be used in powder form to develop latent fingermarks on non-porous surfaces. It was proposed that oleylamine-stabilized gold nanoparticles (Figure 6) deposit onto fingerprints due to the lipophilic interaction with the fatty components in fingerprint ridges.

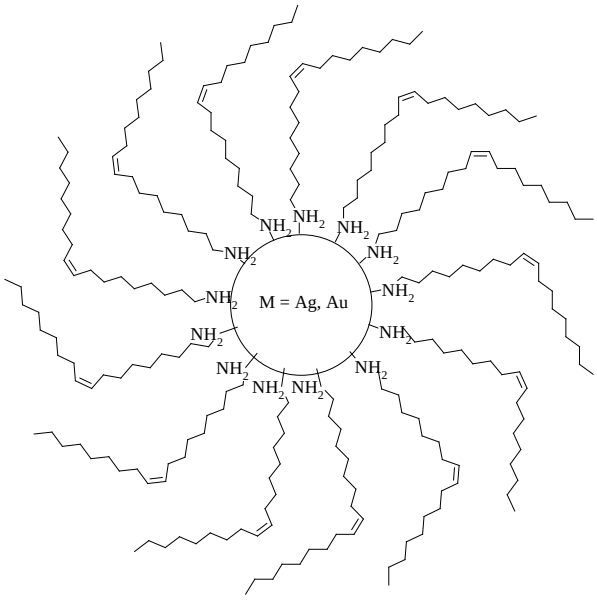

Figure 6. Depiction of an oleylamine-stabilized metal nanoparticle (amine to particle ratio not to scale) [41]

These new powders produced sharp, and more even development of latent fingermarks without background staining on non-porous surfaces compared to conventional powders (Figure 7). SEM images reveal that fingermarks developed by nanoparticles are concentrated in ridge areas with only a minor amount in the valleys areas.

Figure 7. Comparison of Black powder and gold nanopowder on glass. Fresh fingermarks on glass developed by Black powder (left) and Gold nano-powder (right) [41]

3. Metal oxide Particles

In this section we describe nanostructured particles containing metal oxides that have been used for fingermark detection. For some time, conventional (micron-sized) metal oxide powders have been utilized as pigments or colorants, as fluorescent agents, and as fingerprint powders. Much less work has been reported on the use of nanosized or nanostructured metal oxide powders in these applications.

3.1. Titanium dioxide particles

Nanocrystalline titanium dioxide (TiO_2) has been investigated extensively due to its interesting optical, electrical, and photocatalytic properties. Several reports on the application of TiO_2 particles in latent fingermark development have been published. Saunders used a TiO_2 particle suspension to visualize fingermarks on porous and non-porous surfaces [43]. TiO_2 particles were reported to act as nucleation sites for the precipitation of silver from physical developer. The TiO_2 suspension was prepared from a white latex paint containing 44% TiO_2 and

56% Al_2O_5Si and acidified with aqueous citric acid to pH 3. A TiO_2 particle suspension (reported as 21 nm diameter) particle size was also used for comparison. No advantage to using the nanoparticle suspension over the paint-based formulation was reported although limited characterization data about the actual particle sizes was presented. Moreover, the TiO_2 deposition followed by physical developer on fingerprints did not reveal any improvement over the regular physical developer technique.

Wade [44] found that micron-sized TiO_2 particles gave good results developing latent fingermarks on dark, non-porous surfaces where it could be used as a white fingerprint powder or a white small particle reagent. The TiO_2 particles were used in a solution or as a paste. It gave excellent results when used as a substitute for sticky-side powder on both sides of the tape. Bergeron [45] showed that TiO_2 particles in methanol could enhance the visualisation of bloody prints on non-porous and some semi-porous surfaces. The method of application was a two-step spray method first using TiO_2 in a methanol carrier and then rinsing with pure methanol. The developed ridge details on non-porous surfaces were excellent showing tertiary level detail. There were no observable differences between aged (> one-month-old) and fresh bloody prints. For porous surfaces, the results were poor producing a faint outline of the finger or no result. Water can be substituted for methanol although there are some disadvantages such as less contrast and significantly increased processing times. Schiemer *et al* found that titanium dioxide powder suspended in a surfactant solution was the best technique for development of latent fingermarks on the adhesive side of black electrical tape [46]

Polimeni *et al* [47] and Cucè *et al* [48] reported that suspended TiO_2 particles developed latent fingermarks on wet surfaces. Polimeni and co-workers demonstrated that the quality of developed fingermarks depends on the way the surface has been touched and on the time of the contact. The fingermarks on a dust covered plastic bottle were revealed with TiO_2 suspended in detergent solution after washing with distilled water. Williams *et al* [49] described how TiO_2

could be applied in a paste form with a brush, sprayed on as a solution, or evidence could be submerged in the reagent itself to develop prints on both sides of dark coloured electrical tapes and duct tapes. Recently Choi *et al* [50] investigated a new, highly fluorescent dye synthesised using oleylamine combined with a perylene dianhydride compound (see Figure 8).

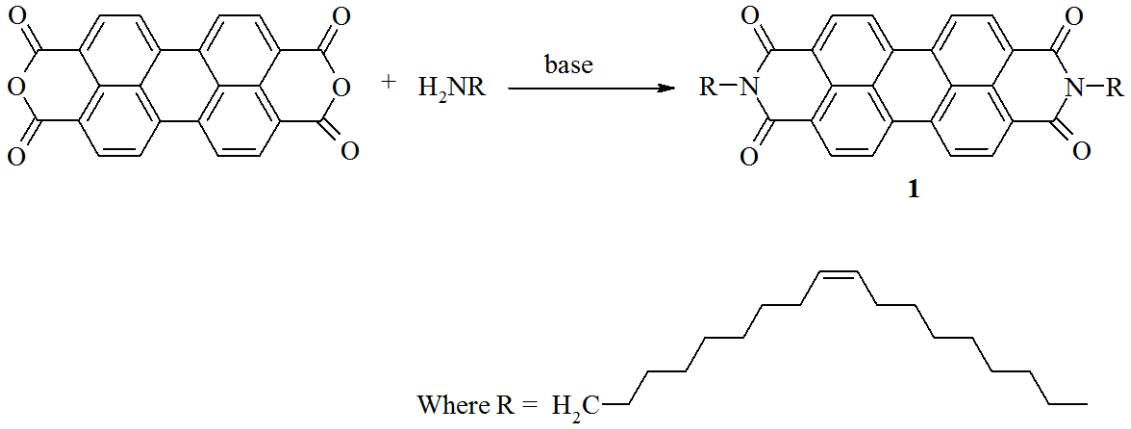

Figure 8. Synthesis of new perylene diimide compound. [49]

The dye was adsorbed onto titanium dioxide nanoparticles for use as a fingerprint detection powder (Figure 9). The new fluorescent powder was applied to latent fingermarks deposited onto different non-porous surfaces and compared with commercial fluorescent powders. Compared with current magnetic fluorescent powders, the new powder was slightly weaker in fluorescence intensity but produced significantly less background development. The nanoparticles developed latent marks with more detail and contrast than conventional-sized powders.

Figure 9. Fresh fingermarks on glass developed with; (left) perylene dye/TiO2 nanoparticles (Degussa brand), and (right) perylene dye/ TiO2 powder in reflection mode under white light illumination. [49]

3.2. Zinc oxide particles

Zinc oxide was evaluated as a fluorescent pigment for the detection of fingermarks on non-porous surfaces by Choi *et al*. [51]. The zinc oxide powders were applied to fresh and aged fingermarks deposited on non-porous surfaces such as glass, polyethylene and aluminium foil. Nanostructured zinc oxide was found to produce clear fluorescent impressions of the latent fingermarks when illuminated with long-wave UV light (Figure 10). Doping of the zinc oxide powders with lithium did not significantly enhance the fluorescence of the developed fingermarks.

Figure 10. Ten-day-old fingermark on glass developed with nanostructured ZnO using the powder and brush technique. Illumination 350 nm, detection 570 nm long pass filter [51].

3.3. Iron oxide particles

Haque *et al* [52] proposed the suspension of iron oxide black powder on non-porous surfaces. The obtained results showed better sensitivity, clarity and contrast than conventional SPR reagents regardless of the age of the prints.

3.4. Europium oxide particles

The rare earth metal europium has a narrow emission band and a long excited-state lifetime (50-100 μs), while most organic fluorescent compounds have broad emission bands and 10-20 ns excited-state lifetimes. These spectral properties can be used to eliminate the background fluorescence of troublesome surfaces in fingerprint detection. Menzel introduced europium to latent fingerprint detection in 1990, treating Ruhemann's Purple and its 5-methoxy- and benzo-analogues with $EuCl_3 \cdot 6H_2O$ [53]. A number of subsequent studies using europium applied to fingerprint development have been reported [54-58]. Figure 11 shows an example of

fingermarks developed with cyanoacrylate fuming followed by staining with a Europium compound.

Figure 11. Fingermarks developed with cyanoacrylate fuming followed by treatment with Europium chelate. Illumination at 350 nm, detection at 610 nm [56].

Menzel *et al* [59] also reported the development of fingermarks using amine-functionalized europium oxide nanoparticles that target the carboxylic acid functionalities of fingermark constituents. The reagent was applied using the SPR technique with an incubation process followed by photoluminescence detection. A time-resolved technique was utilized to successfully suppress background fluorescence.

4. Metal Sulfide Particles

In this section we describe particles containing metal sulfides that have been used for fingermark detection. The majority of work has focussed on molybdenum and cadmium sulfides.

4.1 Molybdenum disulfide

Small particle reagent (SPR) is a suspension of fine particles in detergent solution and may be regarded as a wet powdering technique. Molybdenum disulfide (MoS_2) particles have been used in SPR where upon application they adhere to the fatty constituents of latent fingermarks to form a grey deposit. SPR can be used on range of surfaces including porous or non-porous, adhesive surfaces, and it is especially useful on wet or dusty surfaces [1, 4]. The developed fingermarks can be photographed and lifted in a conventional manner after drying. SPR is generally applied by immersion or spraying; the immersion application method is a reasonably sensitive process but is more effective on fresh fingerprints than older ones. Spray application has been reported to be considerably less effective [60].

SPR was first reported by Morris and Wells in 1979 (according to [4]). Goode and Morris subsequently described a detailed procedure and formulation in 1983 [6]. Frank and Almog [61] proposed that a white SPR formulation based on zinc carbonate powder for dark surfaces. Springer and Bergman [62] reported fluorescent SPR where an ethanolic solution of the dye Basic Yellow 40 (BY40) was added to the SPR stock solution. Excitation at 450 nm and emission at 550 nm was used to visualise fingermarks treated with BY40 SPR on dark or multi-coloured background. Zamir *et al* [63] reported DNA analysis could be conducted after SPR processing of bloody fingermarks.

4.2. Cadmium sulfide nanocrystals

Cadmium sulphide (CdS) nanocrystals and nanocomposites have been investigated for fingermark detection. CdS nanocrystals capped with dioctyl sulfosuccinate in heptane or a

mixture of hexanes developed fingerprints on a soft drink can and aluminium foil previously fumed with cyanoacrylate ester [64]. Examination under an Ar-laser operating in the near UV revealed amply intense luminescence. Unfumed fingerprints on metal, glass, and plastics could not be developed because heptane and hexane tended to obliterate ridge details. On black electrical tape, unfumed fingerprints were developed using a heptane nanocrystal solution [64].

Fluorescent CdS-dendrimer nanocomposites have also been investigated. Menzel *et al* examined the suitability of dendrimers (molecules with branched tree-like structures) as fingerprint reagents using the commercially available Starburst Generation 4 dendrimer, which contains terminal amine groups [65]. The amine groups can react with carboxylic acids found in fingermark deposits and preferential dendrimer attachment to fingermarks was reported. It was not determined if chemical bonding or adherence by physical processes were responsible for the attachment. CdS-dendrimer nanocomposites were prepared by adding solutions of cadmium nitrate and sodium sulphide to a dendrimer solution. Luminescence was blue-green regardless of CdS concentration but luminescent intensity increased with CdS concentration. Fingermarks on aluminium foil, polyethylene (fumed) and paper were developed. In methanolic solution, cyanoacrylate ester fumed fingermarks developed readily however unfumed fingermarks tended to dissolve away. Fingermarks on paper (unfumed) were not detected due to indiscriminate deposition of the nanocomposites. Such long immersion times suggest that a chemical reaction between the amino functionality of the dendrimer and the carboxylic acid groups of the fingermark deposit, or with the cyanoacrylate ester functionality rather than a physical adsorption process.

CdS nanocomposites with a carboxylate terminal-functionalised dendrimer were studied [66]. The carboxylate functional groups can react with amino acids or proteins found in fingermark residue. A successful sequence involved a 1:9 methanol:water solution of the dendrimer with a stoichiometric amount of diimide and heating at 60 °C over night + CdS

incorporation + fingerprint immersion was reported. Fingermark development was very faint without heating. The developed fingerprint luminescence is orange.

As discussed by Sodhi and Kaur, some fingerprint powders may pose a health threat [10]. Cadmium is especially problematic as its toxicity is combined with a half-life in the human body of ~30 years [67, 68]. Thus, the application of these methods in routine casework requires consideration of occupational health and safety issues.

5. Other Metal-containing Particles

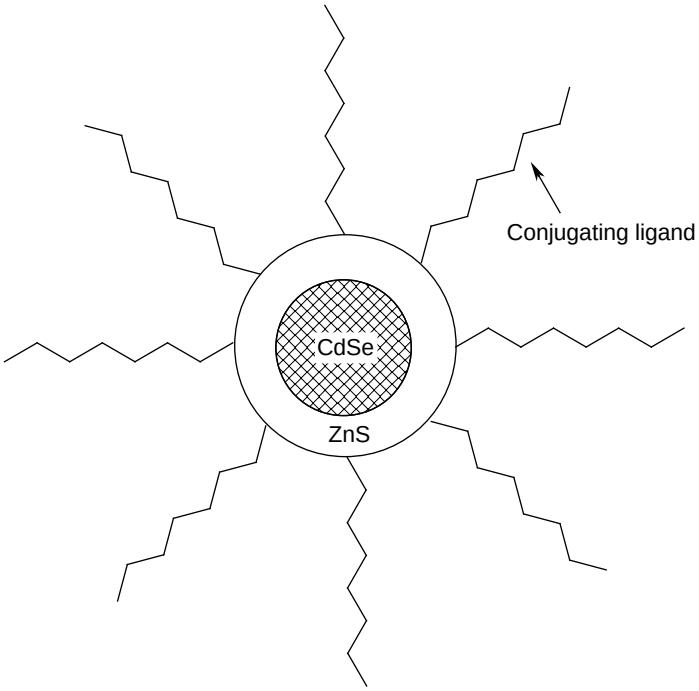

Figure 12. Structure of encapsulated and functionalized CdSe nanocrystal. Re-drawn from [4].

CdSe nanocrystals can be capped with zinc sulfide to reduce aggregation of the nanocrystals and also to serve as a site for attachment of conjugating organic ligands for labelling purposes (Figure 12). ZnS-capped CdSe nanocrystals can be covalently bound to amino acid components of fingermark residue. Development with carboxylate-functionalized nanoparticles has been reported [4]. At room temperature, 24 hrs immersions in a water solution containing in 1μM of

CdSe/ZnS/carboxylate functionalized nanocrystals and in 8 μM of 1-(3-dimethlaminopropyl)-3-ethylcarbodiimide hydrochloride revealed luminescent fingerprints. The utilized nanocrystals produced luminescence with excitation from the ultraviolet to the red, which gives greater flexibility in terms of the excitation light source. Sharp red luminescence was shown at 635nm (red-emitting nanocrystals).

Latent fingermarks have been developed using fluorescent CdSe/ZnS stabilized by octadecaneamine [38] where fingermarks deposited on silicon wafers or paper were immersed in a petroleum ether solution of CdSe/ZnS. Detailed fluorescent prints were obtained on the silicon wafer specimens (Figure 13) but fingermarks were not observed on paper due to heavy background fluorescence under UV illumination.

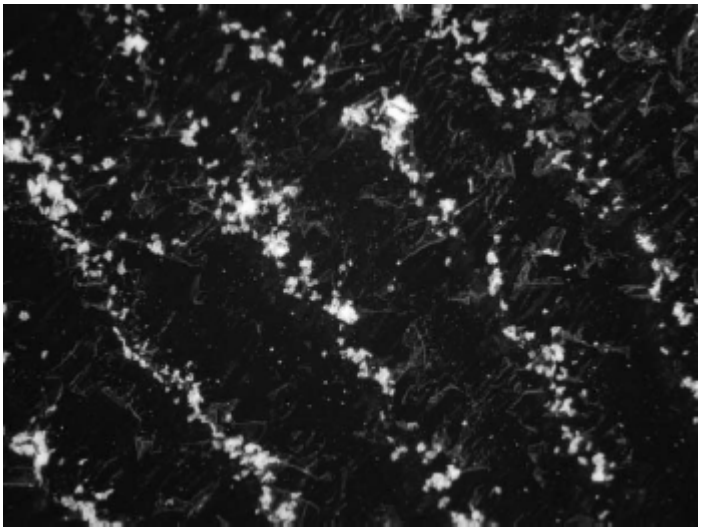

Figure 13. Optical microscope image taken in UV mode of CdSe/ZnS-NPs adsorbed preferentially on fingermark ridges on a silicon surface [38].

6. Conclusion

It is generally accepted that only a subset of all the latent fingermarks present on an exhibit are actually detected. In other words, in routine casework, a non-negligible number of latent

fingermarks probably remain undetected, and consequently cannot be exploited during the investigation. This explains why the demand for improved reagents for fingerprint development has continued in forensic science over the years. Unfortunately, many of the developments are incremental and focus on a small number of techniques. Champod et al. [1] highlighted that "*any significant improvements in detection sensitivity using chemical reagents is likely to require a completely different approach that, as yet, has not been identified*". In this context, nanotechnology has proved to be a promising area of research.

In the broad scientific arena, applications of nanotechnology seem to be only limited by human imagination. In particular, it is generally considered that nanotechnology may lead to the development of new materials and reagents with superior characteristics to conventional ones. Nanotechnology provides new opportunities in surface-based science. Because latent fingermark detection can be broadly seen as surface-based phenomena, it is obvious that nanotechnology is a prime candidate to become the 'completely different approach' mentioned above.

This article reviewed the current status of nanotechnology-based techniques applied to the detection of latent fingermarks. In particular, this review focused on the applications and limitations of techniques relying on metal-containing nanoparticles and nano-structured particles. Some of these methods are yet not sufficiently mature for routine implementation in casework. Further attention and research are required for future improvement and development of nanotechnology-based fingermark detection methods.

References

1. C. Champod, C. Lennard, P. Margot,M. Stoilovic, Fingerprints and Other Ridge Skin Impressions. 2004: CRC Press.
2. R. Pfister, The optical revelation of latent fingerprints. Fingerprint Whorld, 1985. 10: 64-70.
3. P. Margot,C. Lennard, Fingerprint Detection Techniques. 6th ed. 1994, Lausanne: Institut de Police Scientifique et de Criminologie, University of Lausanne.
4. H.C. Lee,R.E. Gaensslen, Advances in Fingerprint Technology. 2nd ed. 2001: CRC press.
5. R. Saferstein,S.L. Graf, Evaluation of a reflected ultraviolet imaging system for fingerprint detection. Journal of Forensic Identification, 2001. 51: 385-393.
6. G.C. Goode,J.R. Morris, *Latent Fingerprints: A Review of their Origin, Composition and Methods for Detection*. 1983, AWRE Report No. 022/83.
7. N. Jones, M. Stoilovic, C.J. Lennard,C. Roux, Vacuum metal deposition: factors affecting normal and reverse development of latent fingerprints on polyethylene substrates. Forensic Science International, 2001. 115: 73-88.
8. N. Jones, D. Mansour, M. Stoilovic, C.J. Lennard, C. Roux, The influence of polymer type, print donor and age on the quality of fingerprints developed on plastic substrates using vacuum metal deposition. Forensic Science International, 2001. 124: 167-177.
9. N. Jones, M. Kelly, M. Stoilovic, C.J. Lennard, C. Roux, The development of latent fingerprints on polymer banknotes. Journal of Forensic Identification, 2003. 53: 50-77.
10. G.S. Sodhi,J. Kaur, Powder method for detecting latent fingerprint: a review. Forensic Science International 2001. 120: 172-176.
11. A.A. Cantu, Silver physical developers for the visualization of latent prints on paper. Forensic Science Review, 2001. 13: 29-64.
12. B. Schnetz,P. Margot, Technical note: Latent Fingermarks, Colloidal Gold and Multimetal Deposition (MMD) Optimisation of the Method. For. Sci. Int. , 2001. 118: 21-28.
13. C.J. Lennard, P.A. Margot, M. Sterns,R.N. Warrener, Photoluminescent enhancement of ninhydrin developed fingerprints by metal complexations: structural studies of complexes formed between Ruhemanns purple and roup IIb metal salts. Journal of Forensic Science, 1987. 32: 597-605.
14. C.A. Pounds, R. Griggs,T. Mongkolaussavaratana, The use of 1,8-diazafluoren-9-one (DFO) for the fluorescent detection of latent fingerprints on paper: a preliminary evaluation. Journal of Forensic Science, 1990. 35: 169-175.
15. M. Stoilovic, Improved method for DFO development of latent fingerprints. Forensic Science International, 1993. 60: 141-153.
16. R.S. Ramotowski, A.A. Cantu, M.M. Joulie,O. Petrovskaia, 1,2-Indanediones: a preliminary evaluation of a new class of amino acid visualising compounds. Fingerprint Whorld, 1997. 23: 131-140.
17. C. Wallace-Kunkel, C. Lennard, M. Stoilovic,C. Roux, Optimisation and evaluation of 1,2-indanedione for use as a fingermark reagent and its application to real samples. Forensic Science International 2007. 168(1): 14-26.
18. S. Wiesner, E. Springer, Y. Sasson,J. Almog, Chemical development of latent fingertips: 1,2-indanedoine has come of age. Journal of Forensic Sciences, 2001. 46(5): 1082-1084.

19. J. Almog, Y. Cohen, M. Azoury,H. T.-R. M., Genipin - A Novel Fingerprint Reagent with Colorimetric and Fluorogenic Activity. Journal of Forensic Sciences, 2004. 49(2): 255-257.
20. G. Levinton-Shamuilov, Y. Cohen, M. Azoury, A. Chaikovsky, J. Almog, Genipin, a novel fingerprint reagent with colorimetric and fluorogenic activity, Part II: Optimization, scope and limitations. Journal of Forensic Sciences, 2005. 50 (6): 1367-1371.
21. M. Stoilovic, C. Lennard, C. Wallace-Kunkel,C. Roux, Evaluation of a 1,2-indanedione formulation containing zinc chloride for improved fingermark detection on paper. Journal of Forensic Identification, 2007. 57(1): 4-18.
22. G. Hodes, When small is different: some recent advances in concepts and applications of nanoscale phenomena. Advanced Materials (Weinheim, Germany), 2007. 19(5): 639-655.
23. B. Wilshire, Advances in fingerprint detection. Endeavour, 1996. 20(1): 12-15.
24. D. Burow, D. Seifert,A.A. Cantu, Modifications to the silver physical developer. Journal of Forensic Sciences, 2003. 48(5): 1094-1100.
25. N. Jones, Metal deposition techniques for the detection and enhancement of latent fingerprints on semi-porous surfaces. PhD thesis, University of Technology Sydney, 2002.
26. D.S. Allman, S.J. Maggs,C.A. Pounds, *The use of colloidal gold/ multi-metal deposition for the detection of latent prints - a preliminary evaluation*. 1992.
27. H. Gregory, *Multi-Metal Deposition An evaluation of storage conditions for colloidal gold solution and the necessity of silanisation in the procedure*, in *Medical Science*. 1998.
28. W. Baschong,Y. Stierhof, Preparation, use and enlargement of ultrasmall gold particles in immunoelectron microscopy. Microscopy Research and Technique, 1998(42): 66-79.
29. R. Cao, R. Villalonga,A. Fragoso, Toward nanomedicine with a supramolecular approach: a review. IEE Proceedings: Nanobiotechnology 2005. 152(5): 159-164.
30. M.J. Choi, K.E. McBean, R. Wuhrer, A.M. McDonagh, P.J. Maynard, C. Lennard, C. Roux, Investigation into binding of gold nanoparticles to fingermarks using scanning electron microscopy. Journal of Forensic Identification, 2006. 56(1): 24-32.
31. G. Festag, A. Steinbrueck, A. Csaki, R. Moeller, W. Fritzsche, Single particle studies of the autocatalytic metal deposition onto surface-bound gold nanoparticles reveal a linear growth. Nanotechnology, 2007. 18(1): 015502/1-015502/10.
32. G. Saunders. *Multimetal Deposition Technique for Latent Fingermark Development*. in *Presented at The International Association for Identification, 74th Annual Educational Conference*. 1989. Pensacola, USA.
33. G.C. Saunders, *Fingerprint detection*. 1989.
34. F. Irrasch. *L'utilasation de l'or colloidal dans la revelation des empreintes digitales: la deposition multimetallique*. in *Seminaire 4eme annee* 1991: Institut de police scientifique et de criminolgie, Universite de Lausanne.
35. M. Hollars,H. Cummings, *Multimetal Deposition*, Latent fingerprint section research team, FBI, Washington DC.
36. A. Becue, C. Champod,P. Margot, Use of gold nanoparticles as molecular imtermediates for the detection of fingermarks. For. Sci. Int., 2006. In press.
37. E. Stauffer, A. Becue, K.V. Singh, R. Thampi, C. Champod, P. Margot, Single-metal deposition (SMD) as a latent fingermark enhancement technique: An alternative to multimetal deposition (MMD). For. Sci. Int., 2007. 168(1): e5-e9.

38. M. Sametband, I. Shweky, U. Banin, D. Mandler, J. Almog, Application of nanoparticles for the enhancement of latent fingerprints. Chem. Commun., 2007: 1142-1144.
39. M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, Synthesis of thiol-derivatized gold nanoparticles in a two-phase liquid-liquid system. Journal of the Chemical Society, Chemical Communications 1994. 7: 801-802.
40. R. Leggett, E.E. Lee-Smith, S.M. Jickells,D. Russell, "Intelligent" fingerprinting: Simutaneous Identification of Drug Metabolites and Individuals By Using Antibody-Functionalized Nanoparticles. Angew. Chem. Int. Ed., 2007. 46: 4100-4103.
41. M. Zhang, A. Becue, M. Prudent, C. Champod, H.H. Girault, SECM imaging of MMD-enhanced latent fingermarks. Chemical Communications (Cambridge, United Kingdom), 2007(38): 3948-3950.
42. M.J. Choi, A.M. McDonagh, P.J. Maynard, R. Wuhrer, C. Lennard, C. Roux, Preparation and evaluation of metal nanopowders for the detection of fingermarks on nonporous surfaces. Journal of Forensic Identification, 2006. 56(5): 756-768.
43. A. Cantu, *Notes on some latent fingerprint visualization techniques developed by Dr George Sanders*. 1996, US Secret Service.
44. D.C. Wade, Development of Latent Prints with Titanium Dioxide (TiO2), Journal of Forensic Identification Journal of Forensic Identification 2002. 52: 551-559.
45. J. Bergeron, Development of bloody prints on dark surfaces with titanium dioxide and methanol. J Forensic Sci 2003. 53(2): 149-161.
46. C. Schiemer, C. Lennard, P. Maynard,C. Roux, Evaluation of techniques for the detection and enhancement of latent fingermarks on black electrical tape. Journal of Forensic Identification, 2005. 55(2): 214-238.
47. G. Polimeni, B.F. Foti, L. Saravo,G.D. Fulvio, A novel approach to identify the prescence of fingerprints on wet surfaces. Forensic Science International 2004. 146s: S45-S46.
48. P. Cucè, G. Polimeni, A.P. Lazzaro,G.D. Fulvio, Small particle reagents technique can help to point out wet latent fingerprints, 146S (2004) S7-S8. Forensic Science International, 2004. 146S S7-S8.
49. N.H. Williams,K.T. Elliott, Development of Latent Prints using Titanium Dioxide (TiO2) in Small Particle Reagent, White (SPR-W) on Adhesives. Journal of Forensic Identification 2005. 55 293.
50. M.J. Choi, T. Smoother, A.A. Martin, A.M. McDonagh, P.J. Maynard, C. Lennard, C. Roux, Fluorescent TiO2 powders prepared using a new perylene diimide dye: Applications in latent fingermark detection. Forensic Science International, 2007. 173: 154-160.
51. M.J. Choi, K.E. McBean, P.H.R. Ng, A.M. McDonagh, P.J. Maynard, C. Lennard, C. Roux, An evaluation of nanostructured zinc oxide as a fluorescent powder for fingerprint detection. Journal of Materials Science, 2008. 43: 732-737.
52. F.W. Haque, A. D.; Milligan, J.; Kerr, F. M, A small particle (Iron oxide) suspension for detection of latent fingerprints on smooth surfaces. Forensic Science International, 1989. 41: 73-82.
53. E.R. Menzel,M.S. Mitchell, Intramolecular energy transfer in the europium-Ruhemann's purple comlex: application to latent fingerprint detection. Journal of Forensic Sciences, 1990. 35(1): 35-45.
54. D.A. Wilkinson,J.E. Watkin, Europium aryl-b-diketone complexes as fluorescent dyes for the detection of cyanoacrylate developed fingerprints on human skin. Forensic Science International, 1993. 60: 67-79.

55. C.E. Allred,E.R. Menzel, A novel europium-biconjugate method for latent fingerprint detection. Forensic Science International, 1997. 85: 83-94.
56. D.A. Wilkinson, A one-step fluorescent detection method for lipid fingerprint; Eu(TTA)3 2TOPO. Forensic Science International, 1999. 99: 5-23.
57. J.P. Caldwell, W. Henderson,N.D. Kim, Luminescent visualization of latent fingerprints by direct reaction with a lanthanide shift reagent. J. Forensic Sci., 2001. 46(6): 1332-1341.
58. E.R.A. Lock, W.D. Mazzella,P. Margot, A new europium chelate as a fluorescent dye for cyanoacrylate pretreated fingerprints-EuTTAPhen: Europium ThenoylTrifluoroAcetone ortho-phenanthroline. Journal of Forensic Sciences, 1995. 40(4): 654-8.
59. E.R. Menzel, J.R. Schwierking,L.W. Menzelm, Functionalized europium oxide nanoparticles for fingerprint detection: a preliminary study. Journal of Forensic Identification, 2005. 55(2): 189-195.
60. H. Office, *Manual of fingerprint development techniques (a guide to the selection and use of processes for the development of latent fingerprints)*. 1998. p. chapter 4.
61. A. Frank,J. Almog, Modified SPR for latent fingerprint development on wet, dark objects. Journal of Forensic Identification, 1993. 43(3): 240-244.
62. E. Springer,P. Bergman, A fluorescent small particle reagent. journal of forensic identification, 1995. 45(2): 164-168.
63. A. Zamir, C. Oz, A. Leifer,B. Geller, The effect of small particle reagent employed as a fingerprint enhancement techniuqe on subsequent STR typing from bloodstains. Journal of Forensic Identification, 2002. 52(6): 691-695.
64. E.R. Menzel, S.M. Savoy, S.J. Ulvick, K.H. Cheng, R.H. Murdock, M.R. Sudduth, Photoluminescent Semiconductor Nanocrystals for Fingerprint Detection. Journal of Forensic Sciences, 2000. 45(3): 545-551.
65. E.R. Menzel, M. Takatsu, R.H. Murdock, K. Bouldin, K.H. Cheng, Photoluminescent CdS/Dendrimer Nanocomposites for Fingerprint Detection. Journal of Forensic Sciences, 2000. 45(4): 770-773.
66. K.K. Bouldin, E.R. Menzel, M. Takatsu,R.H. Murdock, Diimide-enhanced fingerprint detection with photoluminescent CdS/dendrimer nanocomposites. J Forensic Sci, 2000. 45(6): 1239-1242.
67. W. Dabrowski, ed. *Toxins in Food* 2005, CRC Press.
68. N. Lewinski, V. Colvin,R. Drezek, Cytotoxicity of Nanoparticles. Small, 2008. 4(1): 26-49.