Title
Fingermark Detection using Nanoparticles

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1.0. Introduction

The terminology that is used in this chapter clearly differentiates a "fingerprint" from a "fingermark", by following the definitions proposed by Champod and Chamberlain in a recent publication [1]. A fingerprint is defined as "a reference impression from a known sample taken with cooperation and under controlled conditions either using an inking process or an optical device […] Because of their pristine acquisition conditions, prints are a near perfect representation of the friction ridge skin" (from [1]). A fingermark is defined as an impression, generally composed of sweat residues, that is "left adventitiously when one touches an object without gloves or foot wear. By the uncontrolled nature of the deposition, marks are often of varying quality compared to the prints" (from [1]). It should be noted that the distinction between fingerprint and fingermarks was already mentioned in another book [2], with a fingerprint defined as "a record or comparison print taken for identification, exclusion, or database purposes", and fingermarks as "traces left (unknowingly) by a person on an object".

A fingermark constitutes one of the most powerful traces that can be exploited as evidence of identity of source, since it constitutes a partial representation of the ridge skin pattern of an individual's finger. Three kinds of fingermarks may be found during an investigation (being at a crime scene or on a related item): visible, plastic, and latent (invisible). The first two kinds are directly visible to the investigators and require only a camera and optical skills to record them. The last kind is the most common form encountered and corresponds to invisible marks, which require the application of detection techniques to allow their visualization. Their detection constitutes a major and continuous challenge for forensic scientists and investigators. As a consequence, numerous efficient techniques have been developed over several years to detect latent fingermarks on various substrates [3,4]. The books by Lee and Gaensslen and by Champod and coworkers offer two thorough and complete summaries about

fingerprints, the composition of the secretion residue, and the existing fingermark detection techniques [2,5]. It should also be noted that most of the techniques able to detect fingermarks are also suitable to detect marks that emerge from the contact of a surface with other parts of the body presenting papillary ridges (e.g., palms and foot).

Detection techniques are generally classified according to the type and state of substrate and secretion that are targeted. For example, latent fingermarks on porous surfaces may be detected using 1,2-indanedione or ninhydrin (non-exhaustive list); on non-porous surfaces, cyanoacrylate fuming (followed by a staining step) or vacuum metal deposition give excellent results; physical developer or Oil Red O are applied in case of wet fingermarks; and blood-contaminated marks require the use of specific blood-reagents (e.g. Acid Yellow 7 or Acid Violet 17), just to cite a few of several situations encountered. However, a more practical way of classifying the methods, especially when working on the improvement of existing ones or the development of new ones, is to do it by their mode of interaction with the secretion components. If we exclude optical methods from this classification, we can distinguish the methods driven by (1) chemical reactions (e.g., 1,2-indanedione, ninhydrin, and blood-reagents), (2) physico-chemical mechanisms (e.g., physical developer, multimetal deposition, and cyanoacrylate fuming), and (3) physical processes (e.g. powder dusting and powder suspensions). Each interaction mode possesses its advantages and drawbacks in terms of efficiency and sensitivity according to the latent secretions, the nature of the substrate, and various other parameters.

Despite the dozens of techniques currently available to the investigators, some serious issues remain: for example, some surfaces are considered as "problematic", with no or few possibilities to detect fingermarks on them; very faint marks may not be detected using

conventional techniques; and environmental conditions (humidity, heat, light) may have a detrimental effect on the latent residue, decreasing the efficiency of the existing methods. The last 20 years have shown the need to develop new techniques, and to improve existing ones, by widening the application fields and increasing the global sensitivity and success rate of detection. Among the existing improvement possibilities, a promising alternative to conventional techniques exploits nanoparticles or nanostructured materials, which have recently made great strides within forensic research laboratories (see §4) [3,6-8].

The following definitions from the field of nanotechnology (e.g., see references [9-12]) will be applied throughout this chapter:

- Materials with morphological features smaller than 100 nm, in at least one of their dimensions, are referred to as nanomaterials. Nanoparticles constitute a category of nanomaterials that are nanoscale in three dimensions. Nanostructures are nanoscale structures on the surface of materials (not necessarily nanomaterials).
- Nanoscience, or nanotechnology, is that part of science (or a technique) concerned with how nanostructures and nanomaterials are designed, fabricated and applied to specific and well-defined uses. Given such a wide definition, nanotechnology is to be found at the interface between chemistry, biology, physics as well as material science, since it combines synthetic steps and chemical assemblies, solubility and stability issues, optical and spectroscopic properties, as well as biocompatibility issues.
- Nanoparticles are subsets of colloidal particles whose spherical enclosure can range up to 1000 nm (1 micron) in diameter. The terms "nanoparticles" and "colloidal particles" will thus be used preferentially, and interchangeably, according to the context in the following sections.

Since colloidal particles include nanoparticles, what is said about colloidal particles will also be true for nanoparticles, unless otherwise stated.

- A dispersion of colloidal-size particles in a medium whether a gas, a liquid, or a solid is called a colloid (sometimes also a colloidal system, a colloidal dispersion, or a colloidal suspension). Current developments covered here are confined to systems of solid colloidal particles in liquids, also called "sols" (colloidal solutions). Such colloids are usually divided into two types: lyophilic (strong attraction between the colloid medium and the dispersion medium of a colloidal system) and lyophobic (lack of attraction between the colloid medium and the dispersion medium of a colloidal system), depending on how well the system can be redispersed (peptized) after it has dried out [9]. When the solvent is water, these systems are called hydrophilic or hydrophobic, respectively.

- A gel is defined as a porous three-dimensional interconnected solid network that expands throughout a liquid medium. If the solid network is made of colloidal sol particles, the gel is said to be colloidal.

Nanoparticles in the nano-size range exhibit size-dependant properties that differ from those observed in the bulk materials or in atoms (e.g., melting points, magnetic properties, and hardness). This phenomenon is referred as the "quantum size effect" [13-15]. The optical properties exhibited by quantum dots, which are commonly characterized as "zero-dimension" species, are good examples of the "quantum size effect" (quantum dots are discussed further in §2.1.2 and 2.3.2). The confinement of electrons in all three dimensions leads to discrete electronic states, giving the quantum dots specific optical properties such as a strong luminescence, which is not encountered in the bulk material. Another important characteristic of nanoparticles is their very large "relative surface area". In other words, nanoparticles have a much greater surface area per unit mass compared to larger particles or bulk materials (this

subject is further treated in §2.2.1). This constitutes an advantage in terms of catalytic activity and functionalization possibilities. Indeed, since catalytic chemical reactions occur at the surface, a given mass of nanoparticles will be much more reactive than the same mass of material made up of larger particles or as a unique bulk. For example, gold in its bulk state does not present significant catalytic properties whereas gold nanocrystals are known to be good low temperature heterogeneous catalysts [16-18] The origin of this effect is to be found in the fact that the fraction of atoms at the surface of a particle (compared with the ones embedded in its core) increases as the mean particle size decreases.

The properties emerging from the nanometer scale promote research and development of new methods that will benefit from nanomaterials, in various scientific domains. Scientists have recently developed the ability to visualize, engineer and manipulate nanometer-scaled materials. Modern synthetic chemistry permits the creation of particles of almost any structure, either through direct synthesis or through molecular assembly (especially useful when dealing with molecular recognition). The smart combination of all these elements leads to nanostructured materials possessing their own specificities in terms of composition, solubility, optical properties and targeting abilities. Common application fields for nanoparticles cover domains like biomedical, optical and electronic devices, for which the nanoscale size, optical properties and chemical versatility are of prime interest compared to classical (organic) molecules [19-23]. The manipulation and engineering of nanomaterials seem to be a recent activity, but the use of nanoparticles for their specific properties is not new. Numerous historical examples have shown that men were already using nanoparticles centuries ago, mainly as stains. A good example is the Lycurgus Cup, a 4th century AD glass cup illustrating a mythological scene [24]. The main particularity of this cup is its dichroism

(this means that the cup changes its color when it is held up to the light) due to the presence of gold and silver colloidal particles in the glass.

The interest of forensic science research in nanoparticles can be found in the intimate characteristics they feature: the nanoscale particles should guarantee a good resolution in terms of ridge details; the specific optical properties – such as luminescence – should constitute a strong advantage in terms of contrast between the mark and the substrate; and the chemical versatility offered by the surface modifications should provide an increased selectivity for very faint latent fingermarks. All of these properties should combine to lead to an increased success rate of detection compared to conventional existing methods. As to their size, the advantages of using such small elements for fingermark detection can be illustrated by representing an average nanoparticle of ~40 nm by a green pea. At this scale, the width of an average ridge measures almost the width of an American football field. This gives an idea of the great potential of nanoparticles in terms of ridge resolution and representation, when targeting and detecting latent secretions. Of course, this has meaning only if nanoparticles show specificity toward the secretions rather than their surroundings (i.e., inter-ridge regions or furrows). This issue can be addressed by chemically modifying the particle surface in order to increase the specific affinity of the nanoparticles for the ridges (i.e., the secretions) instead of the underlying substrate. Moreover, nanoparticles can be dried and used as powders to detect fingermarks. But a more interesting and safer way of using them is to develop a detection technique based on the use of nanoparticles in solution, in which case they can be modified to increase the selectivity. To reach this goal, it is necessary to understand the way nanoparticles are being formed, how they behave in solution, and how it is possible to tune their chemical and optical properties. All these points are covered in section §2. These are

crucial points to assimilate, since they greatly influence the interaction mechanisms between nanoparticles and the secretion residues.

Finally, the development of a new fingermark detection technique based on the use of nanoparticles involves two distinct stages: first, the choice of the "marker" that will be optically detected (i.e., the atomic composition and the optical properties of the nanoparticle of interest); and second, once the marker is defined, a surface engineering step is usually necessary to tune its behavior so that it will specifically target secretion residues. These two stages may be considered independently. Indeed, markers of different kinds (e.g., quantum dots, silica nanoparticles, or colloidal gold) can share the same targeting strategy if they bear the same outer-surface ligands. The resulting nanomaterials will then target the latent secretions in the same ways, even if they are different in terms of composition of the markers. Similarly, a nanoparticle can be modified so that it will interact differently with the secretions according to the ligand that is added to its surface (the targets can be lipids, amino acids, or other chemical species). By smartly combining these two aspects (i.e. "marker" and "functionalization"), one could offer forensic investigators new, powerful tools for detection. For all of these reasons, this field of research certainly opens a new era in the development of new, original and efficient techniques to detect fingermarks.

Another parameter that plays a major role is the choice of the solvent in which the nanoparticles are synthesized or redispersed (peptized after precipitation). Indeed, aqueous solutions are generally preferred for their lower toxicity and the possibility of being used without the need for working under a fume hood, or applied as a spray at crime scenes, for example. This is the case for colloidal gold in the multimetal deposition process [25-28]. Given the high number of synthesis protocols that can be found in the literature, it is often

possible to synthesize the "same" nanocomposites (if we exclude the nature of the capping ligands, which ensures the stability of the nanoparticles in their medium) either in organic solvents or in water. However, some chemical modifications, such as the addition of hydrophobic ligands on the surface of the nanoparticles, may force their transfer to organic solvents since the resulting nanocomposites are no longer soluble in water [29,30]. The chosen application protocols (e.g., spray at the crime scene, powder dusting, or immersion without the need for a fume hood) will mainly drive the choice for one synthesis route or another.

Besides their application to detect latent fingermarks, nanoparticles can also be used to add security to official documents (e.g., passports), jewellery, and the like, to assure the owner of its authenticity or to decrease the possibility of counterfeits. In Oliver's presentation titled "Digital Security Printing Inks and Toners: Recent Developments in Nano-and Smart-Materials" [31], several examples are provided about the use of quantum dots and other nanoparticles in security and anti-counterfeiting. Other applications of nanoparticles in forensic science include their use in biomedical examinations where visualizing specific bio-organic components in forensic toxicology or pathology is important, and in the fight against terrorism in terms of decontamination of contaminated sites. These applications are beyond the strict context of this chapter and will therefore not be developed further. The readers are invited to refer to the article of Cantu for further information [32].

The next sections give a global overview of commonly encountered nanoparticles, that is, their synthesis and structural/optical properties (§2), how they could be used to detect fingermarks, with the issues that should be answered (§3), and a review of the existing techniques using nanoparticles to detect latent fingermarks (§4).

2.0. Nanoparticles – Structure and properties

Numerous books or publications are currently dealing with nanoparticles and nanoscale materials, in terms of detailed fundamental and theoretical approaches, synthesis, and applications. The reader is strongly encouraged to refer to them if more detailed information about nanoparticles is required. The aim of this section is not to constitute a thorough review of this field since it would certainly be outside of our primary objective. We managed to concentrate our attention on the principal characteristics of interest in fingermark detection techniques based on nanoparticles. The following topics will be covered:

- Synthesis of monodisperse spherical nanoparticles (§2.1)
- Stability of nanoparticles in solution (§2.2)
- Optical properties of nanoparticles (§2.3)
- Surface functionalization (§2.4)
- Health and safety issues (§2.5)

2.1. Synthesis of monodisperse spherical nanoparticles

Nanoparticles can be synthesized from a variety of different materials, in aqueous or organic solutions, leading to versatile compositions, shapes, and properties. All these synthesis procedures can be classified according to only two major approaches: "Top-Down" and "Bottom-Up". The "Top-Down" approach consists in starting with a larger existing structure down-sized by attrition or milling. These physical mechanisms lead to particles of tens to several hundreds of nanometers in size, but generally characterized by a broad size

distribution and several surface defects. This approach is not favoured when nanometer scale structures are to be obtained. The "Bottom-Up" approach consists in building nanoparticles by following a chemical process (element-by-element) through solution-phase colloidal chemistry. More homogeneous particles with few surface imperfections result from this approach. It is thus preferred in the context of nanoparticles of small size. It encompasses two different synthetic processes, namely, thermodynamic and kinetic [33]:

- In the thermodynamic approach, precursor species are placed in a supersaturation state. By doing this, the formation of a second phase (e.g., solid in liquid) occurs to allow the reduction of the system's overall Gibbs free energy [34] (i.e., the system's available energy to do work). This is called the "nucleation step". Once a thermodynamically stable nucleus is created (i.e., when it reaches the critical size at which it will not dissolve again in the surrounding medium), it will start to grow in size by the addition of growth species on its surface. This is called the "growth step", during which the monomers (i.e., the building blocks or atoms) are transported towards the surface of the nucleus and react with it. It should be noted that both nucleation and growth steps can occur simultaneously (if the concentration of precursors is above the supersaturation state), but at different speeds. When the quantity of precursors is no long sufficient to allow the creation of new nuclei, only the growth will continue (Figure 1). Ideally, the nucleation process should be terminated before the system enters into the growth process, so that a uniform (i.e., monodisperse) size distribution is obtained. Nevertheless, according to the nucleation and growth rates, one can obtain monodisperse or polydisperse solutions. A typical example of such an approach is the synthesis of quantum dots in organic solvents, during which reactants are quickly injected in an organic solvent at high temperature [13], leading to an instantaneous burst in the nucleation process which lasts only a very short time due to the sharp decrease in monomer concentration and the fast cooling of the reaction

mixture [35]. Only the growth process remains, and the nanoparticles grow homogeneously in size.

- In the kinetic approach, a limited amount of precursors is available for the growth, or the process is confined in a limited space (e.g., microemulsion or micelles). The growth of the nanoparticles is constrained since it stops when the limited amount of precursors has been consumed or if the space has been filled up with the particle. A typical example of such an approach is the synthesis of nanoparticles (e.g., silica or silver) inside small droplets of water suspended in oil, which is also known as reverse microemulsion [36-38]. Briefly, water nanodroplets are formed in an oil phase (bulk), stabilized by surrounding surfactant molecules, and act as nanoreactors for the formation of nanoparticles. The formation of silica nanoparticles inside the water droplets takes place by hydrolysis of silica precursor molecules using ammonium hydroxide as a catalyst [39]. This process is widely used to obtain nanoparticles with a perfect spherical shape and a very narrow size distribution, with the size of the droplets being controlled by the water-to-surfactant molar ratio.

In forensic science, we can observe that the "Bottom-Up" approach, and more particularly the thermodynamic process, is encountered for the multimetal deposition technique (gold colloids) [25], during the physical developer process (silver nanoparticles) [40], or in recently developed techniques using quantum dots [41-43], silica nanoparticles [44], or zinc oxide nanoparticles [45] (see section §4 for further details).

The scope of this chapter will be limited to the description of three representative nanoparticles:

- Synthesis of gold colloids using reduction agents (§2.1.1),
- Synthesis of semiconductor nanocrystals by thermal decomposition (§2.1.2),
- Synthesis of silica nanospheres following a sol-gel process (§2.1.3).

Two reasons have led to this choice: (1) from a chemical point of view, they are characterized by different nucleation and growth processes, and (2) from a forensic point of view, these nanoparticles are currently focusing research towards the development of new fingermark detection techniques, as it can be seen in §4.

For further information about the synthesis of other kinds of nanomaterials (e.g., various metal or magnetic nanocrystals), or other mechanisms, the reader is referred to existing thorough reviews on this subject [46-48].

2.1.1. Synthesis of gold colloids using reduction agents

The conventional method to synthesize gold nanoparticles in aqueous solution consists of reducing gold (III) derivatives (soluble in water) using reduction agents (e.g., tetrachloroauric acid – $HAuCl_4$ – reduced by sodium citrate). The reduction of the metallic salt leads to the formation of insoluble metallic gold entities that further aggregate to form discrete particles with sizes ranging from a few to hundreds of nanometers. The widely accepted mechanism is a LaMer nucleation-growth model, based on the concept of "burst nucleation" [46,49]. Gold chloride ions are first reduced to atomic Au, up to the supersaturation level of concentration. At a certain moment, many nuclei are being formed at the same time (nucleation step) and most of the other gold atoms begin to get attached to the particles in solution (growth step). During the synthesis, the color of the solution changes from pale yellow ($AuCl_4^-$), to colorless

(gold atoms), dark blue, and finally to ruby red (~20 nm gold nanoparticles). However, a recent study suggests that this nucleation-growth mechanism (according to which each nucleus progressively increases its size until the final colloidal particles are formed) is not compatible with the range of colors that is observed during the synthesis, in particular the transient dark coloration [50]. Pong and coworkers revisited the growth mechanism of gold nanoparticles. They kept the idea of burst nucleation with formation of individual gold nuclei, but they showed that gold nanoclusters of about 5 nm diameter self-assemble during the initial stage of the reaction to form an extensive network of nanowires of ~5 nm diameter (which explains the dark blue intermediate color). The nanowire network grows in size, through addition of gold atoms, until it reaches ~10 nm of diameter. At this point, the structure starts to break up into well-defined spherical particles of diameter ~13-15 nm, due to the adsorption of negatively-charged citrate ions, which induce repulsion between the linked gold nanospheres (Figure 2).

The reduction of gold chloride in aqueous solution was first observed by Faraday, in 1857, using phosphorus as reduction agent [51], and has been further applied, modified and optimized [52-57]. The reduction of $HAuCl_4$ by sodium citrate in boiling water is one of the most currently-used procedures for obtaining monodisperse spherical gold nanoparticles of generally ~10–20 nm diameter, with excellent time-stability (several months to years) [55]. The process of gold nanoparticle formation by citrate reduction has been investigated in detail by Kimling and coworkers, who found a general relation between the gold-to-reductant molar ratio and the final size of the particles [58]. By following the earlier work of Turkevich, they also showed that gold nanoparticles can be synthesized in a wide range of sizes, from 9 to 120 nm, with varying size distributions. The time-stability of colloidal gold can be explained by the formation of an ionic shell around each gold nanoparticle, due to the adsorption of

negatively-charged ions coming from the reaction mixture (mainly from citrate ions). Thus the sodium citrate ions play a double role: the first one as reducing agents and the second one as capping agents, preventing gold nanoparticles in solution from aggregating through electrostatic repulsion (see §2.2.2).

For nanoparticles with diameters below 10 nm, an alternative to the sodium citrate route exists: the sodium borohydride ($NaBH_4$) reduction of gold chloride in a two-phase process (water/toluene) [29]. The nanoparticles synthesized according to this method are capped with thiolated ligands (e.g., alkanethiols R-SH). These colloids can be repeatedly isolated and redissolved in common organic solvents without irreversible aggregation or decomposition [30]. Recently, Hussain and coworkers proposed a way to prepare a near-monodisperse gold hydrosol with diameter size below 5 nm, in a single-step reduction process using $NaBH_4$ and a thio-ether terminated polymeric stabilizer [59]. These particles are readily soluble in both aqueous and non-aqueous solvents. Moreover, the particle size can be controlled by varying the ratio of Au to the capping ligand.

Once synthesized, gold colloids can be used to detect fingermarks (like in the multimetal deposition technique), or can be subsequently surface-functionalized if needed (see §4.4). For further information about colloidal gold (structure, properties, and applications), the reader is strongly invited to refer to the two following excellent reviews on the subject: Daniel and Astruc [60] and Ghosh and Pal [61].

2.1.2. Synthesis of semiconductor nanocrystals by thermal decomposition

Semiconductor nanocrystals are composed of hundreds to a few thousands of atoms only, corresponding to a size range of 1 to 10 nm. These are so-called "quantum dots" or "zero-dimension particles" due to the nanometer confinement exerted in all three dimensions. Such nanoparticles are of a first interest in imaging applications due to their specific photoluminescence abilities, which are directly related to their quantum confinement (see §2.3.1), and the fact that they can be synthesized from a variety of different materials (e.g., CdSe, CdTe, ZnS, HgTe, InP, GaAs, or InAs). During the last decade, various reviews were published on the subject [23,35,46,62-68], as a proof of the strong interest of the scientific community for such nanoparticles.

Two main synthetic routes exist, which differ by the media into which the quantum dots are synthesized, organic solvent or aqueous solution. For both routes, the general growth model of the nanocrystals is based on the same principles as previously described, which is a "Bottom-Up" process initiated by a supersaturation-induced nucleation step followed by a growth step [34]. The choice for one route instead of another has to be made according to the specificities of each one and to the subsequent application of the quantum dots.

- The synthesis in organic media was first proposed in 1993 [13] and is certainly the most popular and the most exhaustively studied route for synthesizing quantum dots [34,35,62,69,70]. From a synthetic point of view, the decomposition of molecular precursors, (i.e., the molecule that will bring the atomic species) is performed by injecting them quickly in a hot coordinating solvent (e.g. 200-360°C). This is the "hot injection" step [13]. As a consequence, the nucleation step will readily start. The high temperature is required to form nuclei because the activation energy for nucleation is much higher than that for the growth of nanocrystals. The role of the organic solvent during the synthesis is two-fold, solubilising the

reactive species and controlling the growth of the nanocrystals by playing the role of surface ligands. Indeed, at high temperature, solvent molecules will continuously bind and unbind from the surface of the nucleus, allowing new atomic species to bind to it and make the nanocrystal grow according to the dynamic induced by the solvent. Currently, tri-octylphosphine oxide (TOPO) and tri-octylphosphine (TOP) are frequently used to play the role of surface ligands, but the possible combinations of precursor, stabilizer and solvent are numerous (see Table 2 from reference [35]). The quantum dots that are obtained are soluble in organic solvents such as toluene, chloroform or hexane. Among the advantages of this synthetic route, we can cite: a narrow size distribution, a high degree of crystallinity, and a high photoluminescence quantum yield – up to 65%. Among the disadvantages of this synthetic route, we can cite: the need for high reaction temperature (i.e., 200-360°C) and the low compatibility of the resulting particles with aqueous solutions. This last point may be problematic in the context of the development of a user-, or environnement-, friendly fingermark detection technique based on water instead of flammable organic solvents. It is somewhat possible to transfer quantum dots synthesized according to the organometallic approach into water, principally through encapsulation, surface modifications or ligand exchange [20,71-75]. However, these processes require additional synthetic steps, which are time-consuming. The solubility of the resulting nanocrystals may not be excellent since the colloidal solutions may be unstable and the quantum yields may be low.

- The synthesis in water is historically the first successful preparation method for semiconductors nanocrystals [76]. However, the first syntheses in water led to quantum dots with low quantum yields, typically 5-10%, which explains why the organometallic route was preferred once discovered. Nevertheless, recent advances in the domain of aqueous synthesis make it a promising alternative to the traditional organometallic one [66,77-81]. It is indeed

possible to increase the quantum yield up to 40-65% through optimization of different parameters involved in the synthesis, for example, the ratio of cadmium to ligand [80,82,83], the surface ligands [66] or the pH [77,80]. Some authors also report obtaining aqueous soluble quantum dots with quantum yields of ~80% using glutathione as capping reagent [84]. The aqueous route is more user-friendly because it is performed at 100°C, compared to ~300°C for the organometallic route, and does not require dangerous materials or solvents. The size distribution is somewhat broader than the one obtained by following the organometallic route, but it can be sharpened through a size-selective precipitation process.

This discussion demonstrates that the synthesis of semiconductor nanocrystals, either in organic or aqueous solution, is well documented and constantly being optimized. Such nanoparticles are stable in solution, similarly to gold colloids, mainly due to the ligand capping that occurs during the synthesis. They can be used as synthesized or they can be further functionalized, if needed. These kinds of particles are promising for use in the field of fingermark detection.

2.1.3. Synthesis of silica nanospheres following a sol-gel process

The sol-gel process is certainly one of the most popular routes for the synthesis of various oxide materials [85], like silica oxide (SiO_2) nanoparticles. The concept of sol-gel consists of creating an oxide network by polymerization reactions of chemical precursors dissolved in a liquid medium [86]. As stated in the Introduction, a sol is defined as a stable suspension of colloidal solid particles within a liquid. Since the particles are generally denser than the surrounding liquid, a stable sol can only be obtained if the dispersion forces are greater than the gravity.

Silica nanoparticles are inorganic oxide particles or organic-inorganic hybrids that can be put in suspension either in aqueous solution or organic solvents. Their synthesis generally consists of a wet chemical mechanism into which reactive precursors (generally silicon alkoxides in alcohol, Si-O-R) are first hydrolyzed, resulting in the corresponding hydroxide species (Si-O-H). The hydrolysis is followed by a (poly-)condensation process between the species in solution through elimination of water, leading to the formation of a network of silicon oxide (Si-O-Si), to finally form a colloidal suspension. The rates of the hydrolysis and condensation steps are important since they will affect the properties of the final product. For example, a slower and more controlled hydrolysis leads to smaller particle sizes. For alkoxides that have low rates of hydrolysis, it is possible to use acids or bases as catalysts to enhance the process. The acids protonate the relatively negative alkoxide molecules, creating a better leaving group and eliminating the need for proton transfer. The bases provide better nucleophiles for hydrolysis [87].

The synthesis of SiO_2 nanoparticles follows either of two major synthetic routes: the "Stöber" or the "reverse microemulsion" methods, which differ by the media into which the nanoparticles are synthesized (bulk water or water-in-oil emulsion, respectively).

- The Stöber method is a wet chemical technique used in materials science and ceramic engineering (metal oxides) to synthesize pure silica nanoparticles or hydrophobic / organic dye-doped nanoparticles [88-91]. This process requires the hydrolysis and the condensation of silica precursors in an alkaline solution of ethanol, water and ammonia. The role of ammonia as a catalyst is to bring the mixture under basic conditions so that three-dimensional structures are formed instead of linear ones. Commonly used silica precursors are silicon alkoxides

bearing four alkyl ligands, like tetraethoxysilane (TEOS) – $Si(OCH_2CH_3)_4$. Functionalized precursors may also be used to confer new capabilities to the particles. For example, Johnston and coworkers proposed to synthesize silica nanoparticles starting from 3-mercaptopropyl trimethoxysilane monomers, $Si(OCH_3)_3$-$CH_2CH_2CH_2SH$, to obtain fully functionalized particles of 1-100 microns in diameter, into which fluorescent dyes can be covalently incorporated post-synthesis [91]. The Stöber method is simple, cheap, and can be carried out in only a few minutes or hours. The silica oxide nanoparticles are characterized by diameter sizes ranging from 50 nm to 2 microns, according to the amount of reagents and catalyst, the nature of the solvent, and the temperature [90]. This synthesis presents the following advantages: a one-pot synthesis carried out at room temperature; the use of ethanol:water mixtures under alkaline conditions, thus avoiding the use of organic solvents; and the possibility to physically trap fluorescent organic compounds in the inorganic network to obtain fluorescent nanoparticles (see §2.3.3). This synthesis suffers from the following disadvantages: the necessity for further filtration and separation steps if monodispersity is required.

- The reverse microemulsion process, also known as "water-in-oil microemulsion (W/O)", is commonly used to synthesize dye-doped or magnetic nanoparticles with a narrow size distribution. It consists of a single-phase system, isotropic and thermodynamically stable, composed of three primary components: water, oil, and surfactant (sometimes, a co-surfactant can be added into the system). The principle is based on the solubilization of surfactants in organic solvents to form spheroidal aggregates, called reversed micelles. In the presence of water, the polar head groups of the surfactant organize themselves around the small water pools, leading to dispersion of the aqueous phase in the continuous oil phase. Those water nanodroplets act as nanoreactors for the formation of nanoparticles. The formation of silica

nanoparticles inside the W/O microemulsion takes place by hydrolysis of precursor molecules using NH_4OH as a catalyst. The formation of nanoparticles is performed in four steps: (1) association of the silicon precursors (e.g. alkoxides) with the W/O microemulsion, (2) hydrolysis and formation of the monomers, (3) nucleation, and (4) particle growth. Ammonium hydroxide acts as a catalyst, by providing the OH^- ions necessary for the hydrolysis of the silicon precursor. In order for hydrolysis to take place, the precursor molecules need to diffuse from the surrounding organic phase into the W/O microemulsion, where NH_4OH is concentrated (due to its polarity). The size of the droplets is mainly controlled by the water-to-surfactant molar ratio (W_0). For example, a W_0 ratio of 10, combined with Triton X-100 as surfactant, can lead to the formation of nanoparticles with diameters of 60 to 70 nm [92]. An increase in the water-to-surfactant ratio changes three parameters: (1) it increases the size of the water pool of the reverse micelles, (2) it increases the number of monomers per microemulsion droplet, and (3) it increases the intermicellar exchange rate due to a decrease in the rigidity of the surfactant film. As a consequence, the size of the obtained nanoparticles decreases [93]. A disadvantage of the reverse microemulsion route is that it requires several thorough washing steps to remove the oil phase and surfactants before being able to recover silica nanoparticles for further applications.

Silica nanoparticles, being synthesized according to the Stöber or to the W/O microemulsion methods, are not readily useful on their own since they are chemically inert, optically transparent and do not possess a natural affinity for finger secretions. It is thus necessary to combine them with a dye (see §2.3.3) and to functionalize their outer surface (see §2.4.3) before being used to detect fingermarks.

2.2. Stability of nanoparticles in solution

In this section, each of the energetic contributions implicated in the stabilization (or destabilization) of colloidal particles in solution will be detailed. This section is thus not directly linked with the use of nanoparticles to detect fingermarks, but could constitute a precious tool for those willing to develop a detection technique based on nanoparticles in solution and facing colloidal instability problems.

2.2.1. van der Waals interactions

Colloidal particles have an extremely large specific surface area (i.e., ratio of the area divided by the mass of an array of particles) due to their small size. To illustrate this, consider the example of a spherical particle of radius R. Its surface area is $4\pi R^2$; its volume is $(4/3)\pi R^3$; its mass is density x volume, and, therefore, the ratio of its surface area to its mass is 3/(R x density). As R decreases, this ratio increases. It means that a collection of colloidal particles has an enormous surface area compared to the single macro-sized particle consisting of all the colloidal particles collapsed into a single unit. The left side of Table 1 shows this for the case of dividing a 1 cm^3 cube into smaller ones. Similarly, if a macro-sized particle is finely divided into tiny colloidal particles of equal size, the overall surface area of the collection of particles is enormous. Consequently, when colloidal particles are dispersed in solution, the collection as a whole has a very pronounced ability to adsorb substances from its surroundings. Such substances include atoms, molecules, ions, and other colloidal particles (whether similar or foreign). In the latter case, when colloidal particles adhere to each other, they coalesce (agglomerate) and no longer remain dispersed (i.e., they become unstable).

How well a substance gets attracted to the surface of a colloidal particle depends on the size of both. How well the adsorbed substance adheres to the surface of the particle depends on the surface energy of the particle:

a. The attractive forces between a colloidal particle and surrounding substances are associated with inter-atomic/-molecular dipole interactions (induced or permanent polarities created in atoms or molecules by the electric fields of neighboring atoms or molecules). Such forces include permanent dipole/permanent dipole interactions (Keesom), permanent dipole/induced dipole interactions (Debye), and induced dipole/induced dipole interactions (London). Collectively these forces are known as van der Waals interactions [94].

b. For two particles of atomic or molecular size separated by a distance R, these interactions are short-range (their energy of attraction has a $1/R^6$ dependence). As with particles getting larger (approaching a plane relative to the smaller particle), the interactions become longer-range (their attraction energy goes from a $1/R^6$ dependence to a $1/R^3$ dependence) [9,10,12,33,95]. As a consequence, the attractive force of a colloidal particle may extend to distances of several nanometers [33], a range comparable or superior to the electrostatic force caused by the interaction of the electrostatic double layers around charged particles (see §2.2.2). This explains why it is sometimes referred to as the "long-range van der Waals force", or "Hamacker force" [9].

c. The particle surface energy dictates how well a substance adheres to its surface. Because surface atoms are bonded only to inner atoms (i.e., there are no atoms above them with which to bond), atom-to-atom bond distances involving surface atoms are shorter than those involving interior atoms. The energy that causes this tightening (tension) is the surface (free) energy and is expressed as energy per area (Joules/cm^2). It can be defined as the excess energy at the surface of a material compared to the bulk. This contribution is important in the case of nanoparticles since the ratio of surface atoms to interior ones increases rapidly as the

size of the particle decreases and reaches the nanometer scale. For example, a 3 nm iron particle has 50% of its atoms on the surface, whereas a 10 nm particle has just 20% and a 30 nm particle only 5% [11]. The surface energy value can be reduced by adsorption (and adhesion) of substances from the surroundings.

d. For an isolated colloidal-sized particle, the surface area is extremely small, as well as the energy of its surface (surface energy [J/cm²] times surface area [cm²]). However, for an entire collection of colloidal particles collectively weighing M grams, the sum of all the surface areas divided by M and the sum of the energy of all the surfaces divided by M are enormous. The adjective “specific” is given to such terms as specific surface area [cm^2/g] and specific surface energy [J/g]. (See the right side of Table 1.) This information is taken in part from Adamson’s Table VII-3 [95]. The differences between his table and Table 1 are: his energy values are in ergs (ours are in Joules), he treats edge energy (we do not), and some of his specific surface area values differ slightly from ours due to the rounding-off process. The vast amount of adsorption and adhesion that occurs among the collection of colloidal particles lowers this overall excess surface free energy (giving the system thermodynamic stability).

When compiling all these contributions, it can be concluded that the nanoparticles have a thermodynamically natural tendency to adhere to each other, so that the resulting size is higher and the specific surface energy lower. This phenomenon is mainly due to the van der Waals attraction forces that play an increasing role as the size of the particle decreases. This aggregation process is logically to be avoided in order to obtain colloidal dispersions that are stable in time. To reach this goal, it is necessary to oppose the van der Waals attraction with other energetic contributions whose role is to repel colloidal particles from each other. This can be done through electrostatic repulsion or steric hindrance.

2.2.2. Electrostatic repulsion

Let us consider colloidal particles of inorganic crystals in aqueous solution. The crystal lattice consists of anions and cations positioned according to their crystal structure. Though such crystals are neutral, they contain localized centers of positive and negative charges on their surface. Such centers include the atoms in the faces, edges, and corners of the crystal. These act as points for surface interaction. For sols of inorganic crystals, there are at least four factors that govern which ions are preferentially adsorbed. These factors are the Paneth-Fajans-Hahn Law, concentration effect, ion charge effect, and size of the ion [96]. When all the other factors are equal:

a. The Paneth-Fajans-Hahn Law states that if two or more types of ions are available for adsorption, then the ions which form a compound with the lowest solubility with one of the lattice ions will be preferentially adsorbed.

b. The concentration effect states that the ions present in greater concentration will be adsorbed preferentially. Furthermore, the quantity of any ions that is adsorbed varies directly with its concentration.

c. The ionic charge effect states that a multi-charged ion will be adsorbed more readily than a singly-charged ion since the strength of adsorption is governed in part by van der Waals attractions which include the electrostatic attraction between the ion and the partial oppositely-charged centers on the crystal surface (the van der Waals-Keesom forces).

d. The size–of-ion effect states that the ion that is more nearly the same size as the lattice ion which it replaces will be adsorbed preferentially.

Consequently, once a nanoparticle is placed in water or in a solvent characterized by high dielectric value, an "electrical double layer" structure will appear. This structure is composed

of two parallel layers of ions (Figure 3), the first one is the surface charge (either positive or negative) and the other one is formed in the liquid to electrically screen the first layer. The surface charge can arise from the adsorption of the surrounding ions, from the dissociation of surface atoms or groups (e.g., protons or hydroxyl groups), from electron transfer, or from other phenomena [33]. The second layer of charge will form because of the electrostatic neutrality of the sol. Counterions will accumulate near the surface to balance the surface charge by an equal, but opposite, charge [86,97]. This second layer is diffuse, because it is composed of non-adsorbed ions, free in the liquid and moving by Brownian motion. The ion concentration decreases progressively as the distance to the particle increases, up to the average concentration in the medium. This causes the electric potential to slowly decay to zero (when moving away from the particle surface). As illustrated in Figure 3, some ions may somewhat adsorb strongly near the surface and build an inner sub-layer (i.e., the Stern layer). The outer part of the screening layer is called the diffuse layer. The double layer may extend up to 10 nm and act like a capacitor (condenser) [94].

It is also important to introduce the concept of "shearing surface", which can be imagined as an envelope lying close to the solid surface and within which the fluid is stationary. When an electric field is applied to a sol, the colloidal particles carrying an electric charge move in the direction of the electrode with the opposite charge. Simultaneously, a certain quantity of the surrounding shearing surface, and the counterions contained in it, move jointly with the particles. A measure of the electrophoretic mobility of the particle and its closely stationary counterions could thus give an idea of the apparent surface charge on the solid particle, as it would be seen by a closely approaching neighboring particle. This leads to a definition a zeta potential (ζ), which is the electrostatic potential at the shearing surface of a particle [98,99].

In general, the ζ potential is smaller than the potential at the surface of a particle, due to the screening effect of the counterions contained in the shearing surface.

The electrostatic interactions between two spherical particles will be influenced by the electric charges adsorbed on the particles according to the electrical double layer structure. As the particles come sufficiently close to each other, the counterion layers start to overlap. It means that the local counterion concentration is higher than it should be for a single particle. Consequently, an osmotic solvent flow is created and the particles undergo some kind of "repulsion force" [86]. This phenomenon directly competes with the van der Waals attraction, which tends to make particles in solution aggregate. The electrical double layer thus plays a role in the stability of the nanoparticles, with respect to coagulation into larger aggregates.

According to the D.L.V.O. theory (from the names of the persons who developed the theory [100,101]), when the attractive forces between two approaching particles (i.e., van der Waals attraction) are balanced with the repulsive forces that could also be experienced by these particles (i.e., electrostatic double layer overlapping), a "repulsion barrier" appears (i.e., a maximum in the potential energy of the interacting particles) and has to be overcome by the two colliding particles to aggregate (Figure 4). If this barrier is not reached, the two particles remain separated in solution. In other words, the combination of the attractive and repulsive forces will determine the stability of a lyophobic colloidal sol. In this context, the zeta potential is generally used as an index of the magnitude of repulsive forces that could be experienced between two particles [99], and in the same way, as an index of a colloidal stability. It is, for example, widely accepted that if a sol has a zeta potential greater than +30 mV or lower than -30 mV, then the electrostatic stability among the particles is sufficient to keep the sol stable [98,102,103]. Moreover, when considering two systems with two different

zeta potential values (all other factors being considered equal), the one with the higher zeta potential value (being towards positive or negative values) is expected to be the more stable with respect to aggregation compared to the other.

However, the repulsion barrier is strongly dependant on the surrounding conditions, for example, ionic strength or pH [94]. For some species in aqueous solutions, the surface charge can be modified according to the pH, whose value is directly related with the quantity of protons or hydroxyl groups in solution. It is the case for oxide species, whose charge is mainly derived from adsorbed protons and hydroxyl groups [86]. In such conditions, it is possible to find a pH value at which a particle exhibits a neutral state (zero-charge) or, in other words, conditions for which the electrical charge density on a surface is zero. This is called a "point of zero charge" (p.z.c.). At the p.z.c., the particle exhibits a neutral zeta potential (the particle remains stationary under an electric field) and is generally accompanied by a rather low stability of the sol and a strong tendency for nanoparticles to flocculate or aggregate (due to insufficiently balanced van der Waals attraction forces). If the pH is set above the p.z.c., the particles will be negatively charged. If the pH is set below the p.z.c., the particles will be positively charged. The reader is referred to the extensive compilation of values published by Kosmulski on this subject for several metal oxides [104]. As an example, p.z.c. values for SiO_2 in water are comprised in the range 2-3.7, and around 6.0 for TiO_2 [99]. This information is crucial to ensure that a solution is stable in time, but also when developing a technique based on the electrostatic attraction between nanoparticles and finger secretions (see §3.2.1).

Another good example of the pH dependence of the stability of a sol is colloidal gold. When gold colloids are synthesized via the sodium citrate metal-reduction route, the sols obtained

generally remain stable for months. This long-time stability is due to the adsorption of tri-negatively-charged citrate ions which preferentially adhere to the metal nanoparticle (via van der Waals attractive forces). As a consequence, the nanoparticles are characterized by a negative charge and are prevented from aggregating through electrostatic repulsion [57]. Faraday, in his experiments, showed that the addition of salts to colloidal gold turned the solution from ruby/red to blue, a sign of the formation of bigger nanoparticles through aggregation of smaller ones due to the increase of the ionic strength of the solution [51]. This can be explained by the fact that an increase in the ionic strength significantly decreases the thickness of the double layer (since the amount of counterions required to balance the surface charge is available in a smaller volume surrounding the particle). As the ionic strength is increased, the double-layer is reduced to a point at which the interparticle potential is attractive, leading to a coagulation of the colloids. For example, it is said that, at ionic strengths greater than 10^{-1} M, the thickness of the double layer is less than 1 nm, which causes the electrostatic repulsion to be insufficient to outweigh the van der Waals attraction [105]. Similarly for gold sols, when the pH is lowered below a limit value (e.g., 1.70), the electrostatic repulsion is no longer sufficient to counter-balance the van der Waals attraction and the sol is irreversibly destroyed by precipitation of large gold aggregates. The origin of this phenomenon is to be found in the neutralization (by protonation) of the citrate ions. As a consequence, the colloidal particles lose their citrate cap, the zeta potential falls below the ±30 mV limit, and the resulting sol becomes unstable (Figure 5). The same phenomenon is observed if citrate ions are replaced by uncharged species [106].

Electrostatic repulsion also plays a role in aqueous solution of CdTe quantum dots. The nanocrystals are generally capped by using thioglycolic acid. This results in an electrostatic repulsion, caused by the negative charge induced by the carboxylic groups, and prevents the

nanocrystals from aggregating. It explains why such colloidal particles are known to be among the most stable (typically, for years) [66].

2.2.3. Steric hindrance

The stabilization through steric interactions consists of placing bulky or long-chained molecules around the nanoparticles to create a physical barrier preventing them from aggregating [33,105]. In colloidal chemistry, dispersions of such macromolecules are called protective colloids [107]. This can be done through the adsorption of polymers that bind through weak physical forces to the surface, or through a chemisorption process, which requires the formation of a chemical bond between the particle and the surrounding molecule. This is typically the case with thiolated molecules which covalently bind around gold nanoparticles to prevent them from coalescing upon drying or after centrifugation cycles [108]. Early literature on colloids describes the conversion of hydrophobic sols to hydrophilic sols by adding to the former macromolecules like gelatine, glue, casein, or gum Arabic so that these get adsorbed by the colloidal particles giving them lyophilic character [109]. Compared to electrostatic stabilization, steric stabilization offers some non-negligible advantages: insensitivity to electrolytes (in the case of non-ionic polymers), equally effectiveness for both aqueous and non-aqueous dispersions, and effectiveness at low and high nanoparticle concentrations. It has to be noted that the steric stabilization plays a major role in non-aqueous solvents, into which electrostatic stabilization is generally ineffective.

The steric hindrance can be combined with the electrostatic repulsion to form what is called an "electrosteric stabilization." [105] The electrostatic contribution may originate from the surface itself (net surface charge) or from the polymer that is attached to the surface. It is

typically the case when charged particles are surrounded by non-ionic molecules, as in the MMD-II process [25]. In this method, Tween 20, a non-ionic surfactant, is added to prevent unwanted background staining, but it also plays a role in the stabilization of the colloidal gold when pH begins to reach low values (Figure 5). This aspect will be detailed in the section §3.2.2.

2.3. Optical properties

In forensic science, techniques leading to photoluminescent fingermarks are generally preferred compared to the ones leading to non-luminescent ones, especially when dealing with dark or complex, multi-colored printed backgrounds. This explains the success of 1,2-indanedione and 1,8-diazafluoren-9-one (DFO) for detecting latent fingermarks on porous surfaces, or the use of luminescent dyes after cyanoacrylate fuming [2,3,110,111].

Photoluminescence is defined as the generation of light from a compound after it has been excited by photons. It can further be divided into fluorescence and phosphorescence. Both are broadly based on the same excitation-emission processes but phosphorescence presents a much longer excited state lifetime, which leads to longer emission of light compared to fluorescence. It should be stressed that the emission wavelength is directly related to the energy of the emitted photons, itself related with the band gap energy (i.e., the difference of energy between the empty conduction band and the electron-filled valence band in solids). Photoluminescence is of a particular interest when the contrast between what should be observed and the underlying substrate is not visible to the naked eye.

In bio-imaging, scientists take full benefit from bioconjugated luminescent nanoparticles to develop imaging techniques presenting an excellent contrast between the elements to be observed [20,22]. It seems logical that forensic scientists take full benefit from luminescent nanoparticles in the development of new fingermark detection techniques. Among the wide variety of existing nanoparticles, some are luminescent by nature (e.g., quantum dots), and others become luminescent after physical entrapment of organic fluorophores in their structure (e.g., silica nanoparticles).

The following sections will focus only on a limited number of nanoparticles of interest.

2.3.1. Gold nanoclusters

Gold nanoparticles are not commonly known for their luminescence properties, but more for their strong surface plasmon absorption associated with the most commonly used colloidal gold solutions (with diam. > 5 nm). Nevertheless, it has been shown that gold nanoclusters of very small sizes (few tens of gold atoms per cluster only), stabilized in aqueous solution by organic ligands or polymers, could behave as molecules and present some photoluminescence behavior in the infrared and visible range. Link and coworkers reported the observation of visible to infrared luminescence for a 28-atom gold cluster stabilized by glutathione [112]. Wilcoxon and coworkers reported a visible luminescence (i.e., 440 nm) of small gold nanoclusters (diam. 5 nm) formed in water by sodium citrate reduction [113], once excited with a 230 nm light source. Only the smallest-sized nanoclusters showed significant photoluminescence quantum yield, with the photoluminescence totally disappearing for gold nanoparticles of bigger sizes. Nevertheless, the associated quantum yields were extremely low (i.e., 3.5 x 10^{-3} [112] and 10^{-4} to 10^{-5} [113], respectively). More recently, some researchers

reported strong fluorescence behavior of small gold nanodots (diam. < 2 nm) encapsulated in a dendrimer [114]. A blue emission at 450 nm has been recorded when illuminating the solution at 384 nm, with measured quantum yield of ~0.4, which is much higher than previously observed luminescence intensities. Bao and coworkers reported the synthesis of gold nanoclusters utilizing a hydroxyl-terminated poly(amidoamine) or PAMAM dendrimer as a template and ascorbic acid as a reductant [115]. The nanoclusters were characterized by blue, green, and red emissions, with quantum yields ranging from 0.09 to 0.38.

As a conclusion, the low quantum yields initially observed for gold nanoclusters prevented them from becoming good fluorophores. Some recent observations showed that higher quantum yields (up to 0.4) could be obtained when stabilizing gold nanodots with dendrimers. Nevertheless, the necessity to synthesize, purify, and stabilize gold nanoclusters of very small size considerably limits their application in the field of fingermark detection. The luminescence of gold nanoclusters remains thus anecdotal and represents no particular appeal in this application, at the moment.

2.3.2. Quantum dots

The size of the quantum dots directly influences their optical properties. The origin of this specificity is to be found in quantum chemistry and in the combination of atomic orbitals [116,117]. Briefly, when a particle reaches dimensions in the range of the nanometer scale, the energy levels (i.e., bonding and antibonding) do not exist anymore in terms of bands of energy but are quantized into discrete values. This phenomenon is accompanied with an increase in the effective band gap of the material with decreasing crystallite size and is called the "quantum size effect" [13-15]. For example, the quantum size effect can be observed with

a CdS nanocrystal when its size is comparable or below 5-6 nm (which corresponds to 3000-4000 atoms) [14]. As a result of this quantum confinement, a hypsochromic shift of the absorption and emission spectra can be observed as the particle size decreases [15,118]. In other words, for the same atomic composition, both the optical absorption and emission of quantum dots shift to the blue (higher energies) as the size of the dots gets smaller (Figure 6). When modifying the atomic composition of quantum dots and their size, it is possible to obtain spectral emissions ranging from UV-blue (e.g., ZnS, ZnSe, and CdS) to the near-IR (e.g., PbSe, HgTe, and InAs), including the visible spectrum (e.g., CdSe, CdTe, and InP) (Figure 7). Moreover, overcoating nanocrystallites with higher band gap inorganic materials (to form the so-called "core/shell" structures) results in an improvement of the photoluminescence quantum yield [119]. On this subject, Lupton and Müller propose a thorough review of the recent progress made in studying the spectral characteristics of CdSe nanocrystals [120].

When compared with conventional, molecular organic dyes, quantum dots offer superior optical properties such as: (1) the possibility to tune the fluorescence emission wavelength as a function of the nanoparticle diameter, (2) broad excitation spectra combined with narrow emission spectra, and (3) high fluorescence quantum yield [121]. The second point means that the excitation of a range of quantum dots of different sizes can be performed at a single excitation wavelength, with each quantum dot emitting according to its specific narrow range of emission wavelengths. Despite the fact that the manipulation of nanocolloids in biological environments may be more complicated, the optical advantages of quantum dots over classical organic dyes explain their success in biological domains like cellular imaging and labelling [20,21,71,122-124], especially in multicolor imaging [125-127] or infrared imaging [128]. As an illustration of the optical superiority of quantum dots to organic dyes, CdSe/ZnS

quantum dots were described as being 20 times as bright, 100 times as stable against photobleaching (i.e., the total loss of fluorescence through destruction of fluorescent molecules), and one-third as wide in spectral linewidth in comparison with organic dyes such as Rhodamine [129]. In addition to this, large Stokes shifts (> 100 nm) and high molar extinction coefficients (i.e., the measure of how strongly a chemical species can absorb light at a given wavelength) make quantum dots promising nanoparticles to be used in the context of fingermark detection.

It should be noted that anti-Stokes photoluminescence has been observed in some semiconductor nanocrystals. This means that the emission of light is observed at shorter wavelengths than that at which the material has been excited. This phenomenon is also called an "up-conversion process" and is reviewed by Rakovich and Donegan [130]. The up-conversion process can be of interest in the domain of fingermark detection by avoiding the background fluorescence of some substrates that considerably decreases the contrast between the mark and the substrate upon illumination [131].

2.3.3. Silica nanospheres

Silica nanoparticles differ from quantum dots, or from other self-luminescent nanoparticles, in a sense that they are optically inert on their own. Nevertheless, one of the advantages of the sol-gel process is that the reactions are performed at low temperature, permitting organic and inorganic species to coexist within the same matrix. An organic dye molecule can thus be easily added to a sol-gel liquid solution, resulting in its encapsulation in the porous oxide matrix. Such entities are called "dye-doped silica nanoparticles". Each nanoparticle is able to encapsulate tens of thousands of fluorescent dye molecules in their silica matrix, providing

highly amplified and reproducible signal. This also allows the dyes to be isolated from the outside environment (oxygen and water), resulting in an increased photostability and emission quantum yield, and a decreased photobleaching phenomenon [92]. Consequently, the luminescence of dye-doped silica nanoparticles may be up to several tens of thousands of times more intense than those based on single organic fluorophore [132]. Organic dyes are generally preferred to inorganic ones due to a relatively higher quantum yield [133], for example, 60-70% for inorganic compared to >90% for organic dyes [22]. In bio-imaging applications, silica has been identified as being more appropriate than polymers since it is not subject to microbial attack and there is no swelling or porosity change with a change of pH [134]. For all these reasons, and in addition to their excellent bio-compatibility as well as the possibility of easily tuning their surface properties, dye-doped silica nanoparticles are hailed as highly promising biological markers [103,132,133].

Several possibilities are offered to scientists willing to encapsulate fluorescent dyes. This can be done during the nanoparticles' formation, using the Stöber synthesis [90,135,136] or the reverse microemulsion [92,133,137-142]. However, the incorporation of dyes into the silica matrix is challenging since the hydrophilic environment of silica does not favour the entrapment of hydrophobic molecules. Consequently, one of the major problems with fluorescent nanoparticles is the leakage of dye molecules from the silica nanoparticles after dispersion in an aqueous medium (while performing bioanalytical tests, for example). Several possibilities exist to solve this issue:

a. The use of polar dyes so that the electrostatic interactions are maximized with the negatively-charged silica matrix [90,133,137-140,142],

b. The use of dyes of a sufficiently large size, preventing them from leaking outside of the silica nanoparticle through the pores [133],

c. The combination of the organic dye with a hydrophilic moiety to make it water-soluble (e.g. dextran Mw 3000) [133],

d. The use of a hydrophobic silica precursor that would place itself inside the structure and promote hydrophobic interactions with the dye [44,143],

e. The covalent binding of the dye to the silica matrix [89,91,136], followed by the addition of a supplemental silica shell around the dye-doped core to increase the photostability of the organic dye (and, by the same way, the fluorescence of the whole nanoparticle)[144,145].

About the electrostatic interactions, Zhou and Yip studied the difference in behavior between a negatively-charged dye (i.e., fluorescein) and a positively-charged one (i.e., Rhodamine 6G) once inserted in a silica hydrogel [146]. They observed that the strong Coulombic interactions between Rhodamine 6G and the negatively-charged silica surface render them immobile, permanently embedded inside the silica matrix as the particles (or the network) grow in size. On the contrary, the electrostatic repulsion between fluorescein and the silica matrix render it extremely mobile in the hydrogel.

Some authors observed a slight shift of the emission spectra of the encapsulated dyes (from reverse emulsion synthesis) compared to the dyes in solution [93,137,138,140,142,147]. Additionally, it is possible that entrapped dyes exhibit an excimer-like emission in place of a monomeric optical behaviour, especially in case where the dye concentration was high during the doping process [148].

2.4. Surface functionalization

One of the biggest advantages that nanoparticles offer compared to organic fluorophores is that they can be functionalized (on their outer surface) almost without interfering with their

optical properties. The addition of organic chains or molecular groups therefore modifies their physico-chemical properties and offer new possibilities in terms of solubility in aqueous or organic solvents, affinity for some specific molecular target, or enhanced stability. This mechanism is widely used in biosensing or biomedical imaging, where nanoparticles should be biocompatible (i.e., stable and compatible with physiological conditions), a process also known as "biofunctionalization" [20,22,124,149-155]. Biofunctionalization is defined as the linkage of biomolecules to nanoparticles or in designing appropriate biocompatible coatings. The coupling must be stable and the surface modification should not modify the photoluminescent properties of the nanoparticles. In the context of fingermark detection, the tendency is not really oriented towards grafting of biomolecules (e.g., proteins affording catalytic activity), even if some publications refer to antibody-antigen recognition of latent fingermarks [156-163]. It is more limited to the addition of organic chains to promote hydrophobicity (e.g., alkanes) or to add simple functional groups (e.g., carboxylic acid or amino group), as illustrated in Figure 8.

A great freedom is offered in terms of outer functionalization and the choice for a ligand or a biomolecule mainly depends on what goal is to be reached. As illustrated in Figure 8, the nature of the nanoparticle itself will also play a role, but less major in this case since it will be mostly be related with the choice for a specific anchoring group (having little influence on the terminal functionalization and the optical properties). The same functionality can consequently be added to various nanoparticles (e.g., colloidal gold, quantum dots, and silica nanoparticles to keep with the examples chosen before), but the functionalization process will differ for each nanoparticle, due to its intrinsic nature, as discussed below.

2.4.1. Functionalization of gold nanoparticles

In the case of gold nanoparticles (as well as for silver nanoparticles), gold atoms on the surface of the particle are coordinately unsaturated (i.e., unoccupied orbitals are available for nucleophiles to donate electrons). Thiol or amino groups do constitute good anchoring groups, given their nucleophilic behaviour. This explains why the most common coatings for metal nanoparticles are ω-substituted alkanethiols, $HS-(CH_2)_n-R$. Such molecules spontaneously chemisorb on the metal surface to create an interface between the nanoparticles and the surrounding environment (Figure 9). Alkanethiols generally permit the creation of well-defined coverings in terms of composition and structure, as well as in terms of chemical and physico-chemical properties through the terminal functional groups ("R").

The mixing of gold nanoparticles with molecules (or biomolecules) bearing thiol or amino groups leads to a spontaneous binding and formation of self-assembled monolayers onto the metal surface, without the need for harsh reaction conditions (temperature, pressure). Even if successful, self-assembled monolayers were reported to be created within minutes of reaction [164]; however, it is generally accepted that a longer deposition period (e.g., several hours) facilitates a monolayer with a high degree of order by enabling surface rearrangement. Another aspect of the functionalized gold nanoparticles is the possibility to remove the solvent, drying the nanoparticles, and still keeping the ability to resolubilize them later (which is not the case with unmodified gold nanoparticles)[29].

The ligands of water-soluble, citrate-capped gold nanoparticles can be easily displaced and replaced by other ones [165]. The functionalization can also directly be performed during the reduction process leading to the formation of functionalized gold nanoparticles. This is the case in the procedure described by Brust and coworkers [29,166], which permits alkanethiol-

or alkylamine-ended ligand-protected gold nanoparticles to be obtained that are mainly soluble in organic solvents. Similarly to Brust, Templeton and coworkers described the obtaining of water-soluble, ligand-protected gold nanoparticles, using tiopronin [167,168]. The solubility of the ligand-capped gold nanoparticles is highly dependent on the choice of the capping ligand. Zheng and Huang distinguished three kinds of ligands according to their ionic behavior (i.e., strongly ionic, weakly ionic, and neutral) allowing one to determine in which mediums such capped gold nanoparticles will be soluble [150].

The created "metal-S" or "metal-N" bonds are quite strong, almost covalent, ensuring by the same way a good stability of the functionalization. Nevertheless, these bonds can still be broken through ligand exchange by the addition of a second one, presenting an increased affinity for the metal surface (e.g., another thiolated molecule). The replacement of existing Au-X (X= P, S, N) bonds with other ligands leads to homogeneous or heterogeneous monolayers [169]. Compared to direct synthesis, the ligand exchange reaction introduces a versatility aspect to the functionality of nanoparticles in solution. However, it also adds supplemental synthetic steps and it is sometimes difficult to control the composition of the final monolayers.

Since biomolecules bear outer amino and thiol groups, coming from amino acid side chains, they can also present a spontaneous affinity for gold nanoparticles [152,155]. For example, citrate-capped gold nanoparticles, which are water-soluble, can be bioconjugated by a ligand exchange process using thiolated proteins [170]. Lévy and coworkers have functionalized citrate-capped gold nanoparticles with pentapeptides to obtain stable, protein-like gold nanoparticles [171]. The same work has been performed using silver nanoparticles, to increase their stability in aqueous solution [172]. Similarly, thiol- or amino- containing amino

acids can also spontaneously bind to the gold surface to form self-assembled monolayers, as shown for cysteine [173], lysine [174,175], or tryptophane [176]. Another possibility for immobilizing biomolecules on gold and silver substrates through covalent or non-covalent interactions involves using carboxylic acid thiol derivative coatings (e.g., HS-R-COOH, where "R" is a hydrocarbon linker). For example, 2-mercaptosuccinic acid (MSA) [108,177,178] or mercaptoproprionic acid (MPA) [179] can be successfully used as a biocompatible coating for protein's or enzyme's adsorption / immobilization.

The functionalization of gold nanoparticles by silica creates a shell that is chemically inert and optically transparent (for gold imaging, for example) [180-182]. However, gold metal has very little affinity for silica because it does not form a passivating oxide film in solution. Moreover, the ions that stabilize the gold nanoparticles in solution (e.g., sodium citrate ions) are generally vitreophobic (silica has no affinity for them). To circumvent this problem, it is necessary to use silane coupling agents as surface primers, that is, molecules bearing a Si atom and $–NH_2$ or –SH functions at their extremities to ensure gold binding (e.g., (3-aminopropyl)trimethoxysilane, or APTMS). Such silane coupling agents are generally added during a post-functionalization process, but can also be introduced during gold nanoparticle synthesis [183]. It should be noted that if the silica layer formed in water is too thin, the van der Waals forces are still very strong and can induce flocculation [184].

Finally, isothiocyanate groups (S=C=N-) are also able to bind to gold nanoparticles, as it has been shown with fluorescein isothiocyanate (FITC)[182]. When FITC is added to gold sol, the suspension remains stable for months. The electrostatic repulsion between the negatively-charged particles (anionic form of FITC at neutral and basic pH values) prevents the aggregation of the particles. As a proof of the functionalization, the FITC fluorescence band

(518 nm) overlaps with the gold surface plasmon band (520nm), leading to an effective energy transfer from the excited molecule to the gold surface (quenching). This transfer is effective, even at 1 nm from the gold surface.

2.4.2. Functionalization of quantum dots

A surface functionalization is already performed during the synthesis of quantum dots, due to the coordinating ligands (being in water or in organic solvents). This is the case with the use of thioglycolic acid, leading to carboxylic acid-surrounded, water-soluble quantum dots (the anchoring group being a thiol) [77,81]. Nevertheless, this initial coating is not always adapted to the application for which the quantum dots are synthesized. For example, their use as biomarkers requires their combination with biomolecules, generally through the addition of functional groups or reactive sites on their outer surface [23,67,68,122]. This can be done through covalent coupling using amines or thiolated molecules, or by surrounding the quantum dot core with a silica shell [185]. Thiolated biomolecules can also replace the thiolated ligands present on the quantum dot surface, through a ligand exchange process. Another possibility involves grafting carboxylic groups to the quantum dot surface and then to couple them with amine groups from proteins [129] or antibodies [186].

Non-covalent coupling, hydrophobically- or electrostatically- driven, is also possible. Some examples exist, like negatively charged CdTe quantum dots capped with 3-mercaptopropyl acid, then coupled at pH 7.3 with papain (an enzyme) which is positively-charged at this pH value [187]. Positively-charged protein domain (pentahistadine segment) can also bind with negatively-charged alkyl-COOH-capped quantum dots. For example, Goldman and coworkers showed that avidin (a positively-charged protein) can adsorb tightly to quantum dots modified

with dihydrolipoic acid, since it gives a homogeneous negative charge on the quantum dot surface [188].

2.4.3. Functionalization of silica nanoparticles

In the case of silica nanoparticles, one of the most popular strategies consists in taking benefit of the chemistry of their surface silanol (i.e., Si-OH) and siloxane (i.e., Si-O-Si) groups. The addition of supplemental siloxane layers (bearing specific functional groups) around existing nanoparticles in solution is easily performed by using an organosilane, or a functionalized alkoxysilane bearing a non-hydrolyzable Si-C bond (e.g., $X\text{-}(CH_2)_n\text{-}Si\text{-}(OR)_3$, where X is the functionality to add). Similarly to the formation of the nanoparticles, the combination of hydrolysis and condensation steps permits to create an additional silica layer around the existing nanoparticles. However, instead of bearing silanol groups (Si-OH), this new layer will exhibit organic chains bearing functionality on their other end. As an example, a common functionalized alkoxysilane is the (3-aminopropyl)-triethoxysilane (APTES) which leads to amino-functionalized silica nanoparticles, as illustrated in Figure 9. This kind of functionalization is extremely stable since numerous covalent bonds are formed between the ligands and the nanoparticle. It is a common way to modify bare silica nanoparticles with a huge variety of organic chemical functions [154], such as thiol [90-92] [189], amine [89,137], or carboxylate groups [22,139,141], to only cite the three major chemical functions usually implicated in fingermark detection mechanisms.

Functionalization of silica nanoparticles can be done in the same mixture that was used to synthesize them (we talk about "one-pot synthesis") or after the nanoparticles have been synthesized (we talk about "post-functionalization", "postgrafting", or "two-step process").

Functionalization can also be performed through the covalent addition of ligands or precursors, or achieved by the (electrostatic) adsorption of (charged) ligands on the surface of the nanoparticles. According to the functional group that has been added on the nanoparticle surface, a variety of subsequent surface modifications and immobilization procedures can be used to couple the functionalized silica nanoparticle with (bio)molecular groups [139,154]. When linking a probe biomolecule, it becomes possible to target oligonucleotides, enzymes, antibodies or other proteins of interest. For example, Qhobosheane and coworkers used an amino-terminated chain to initiate the bioconjugation of silica nanoparticles [141]. Santra and coworkers modified the surface of luminescent silica nanoparticles using TSPDT (a primary amine group with a long chain), and further with antibodies [138]. Hydrophobic chains can also be added on the surface of the silica nanoparticles, such as octadecanol [89] or lauroyl chloride [137], so that they can be dispersable in organic solvents (e.g., cyclohexane or chloroform). The use of amino-functionalized (dye-doped) silica nanoparticles has also allowed them to be coated with nano-sized metal colloids, to finally form a homogeneous gold [145,190] or a silver [135] shell around them.

These three sections were aimed at providing to the reader with an overview of the wide possibilities offered by the functionalization of nanoparticles. Combining optical properties with specific functionalization constitutes the main challenge in designing a new fingermark detection reagent. In addition, solubility and solution instability issues are parameters that need to be addressed when trying to set up an optimal application protocol.

2.5. Health and safety issues

It seemed necessary to introduce the potential risks, in terms of environmental and health and safety issues, which could arise when working with nanoparticles. Indeed, the increasing use of man-made nanomaterials may lead to possible health impacts [191] or environmental dangers [192], that were not considered or encountered until now. Recently, several studies and publications have dealt with these concerns, especially since commercial applications of nanoparticles has increased (e.g., cosmetics, clothes, medicine, water filtration, among others) and will certainly continue to increase in the upcoming years [193-198].. There is growing concern of the potential health hazards of nano-sized materials because they may interact adversely with biological systems at the cellular and sub-cellular level. Questions have been raised about their potential toxicity, their long-term secondary effects on human beings or their biodegradability.

Due to their small size, nanoparticles may penetrate the body (through skin, ingestion or inhalation) or cell membranes, and interact further with biological systems [195,199] and cell life cycle [197]. Rothen-Rutishauser and coworkers showed, for example, that size was the most important factor (compared to the charge or the nature of the nanoparticles) that influenced the ability of nanoparticles to penetrate inside red blood cells by mechanisms not related to phagocytosis or endocytosis [200]. Moreover, some engineered surface coatings may also enhance the ability for nanoparticles to penetratenatural organic barriers. The main worries expressed towards the penetration of nanoparticles in human bodies are related to their high surface-to-volume ratio, which makes of them very reactive or catalytic species. This may lead to the formation of reactive oxygen species, for example, which may induce pulmonary inflammation, oxidative injury, or cytotoxicity, even if the same material is inert in its bulk form [191,196,199]. It is also currently recognized that the potential toxicity of nanomaterials cannot be deduced from the toxicity of the corresponding bulk material, since

new properties may emerge with nanoparticles compared to larger ones. For example, the toxicity of asbestos mainly comes from its shape (sharp needles), not from its elemental composition. This explains why carbon nanotubes are now compared to asbestos in terms of risks in inducing inflammations (e.g., reactive oxygen species generation, lipid peroxidation, oxidative stress, or lung inflammation) [196,201]. However, Nel and coworkers showed that no conclusive data indicating that toxic effects related to nanomaterials currently exist or that they may become a major problem that could not be addressed by a rational scientific approach [196]. Indeed, only a limited number of nanomaterials, at high doses, have shown to induce toxicity in tissue cultures and animal experiments [194]. However, potential health risks due to the use of nanoparticles cannot be neglected.

The issue of the risks related with the (industrial) synthesis of different nanomaterials (e.g., carbon nanotubes, ZnSe quantum dots, or TiO_2 nanoparticles) has also been thoroughly studied in terms of volatility, carcinogenicity, flammability, toxicity, and persistence of the used materials, and compared with the impact of other manufacturing processes (e.g., lead-acid batteries, aspirin, wine, or polyethylene production) [202]. The authors concluded that there does not appear to be any unusual risks related to the production of the studied nanomaterials compared to other common processes.

In the context of the development of new forensic applications based on nanoparticles or nanomaterials, a proactive approach is thus required from researchers. Choices have to be made when choosing the nature and chemical composition of the nanoparticles of interest, as well as in their application protocol, so that they are the least toxic possible for the users (investigators or laboratory workers). For example, applying nanoparticles in solution is certainly a safer technique than dusting with a nano-based powder at the crime scene, due to

their dilution and the fact that in solution they are less likely to be released in the atmosphere (even if there is still a possibility to form aerosols). Forensic investigators should, in any event, wear proper protective equipment to prevent any further risk associated with a long-term exposure to these materials. However, these safety precautions are not limited to nanomaterials and are valid for all reagents and organic solvents that are currently used in commonly applied fingermark development techniques.

The next section provides details concerning the secretions contained in latent mark residues, since these substances will be the target of reagent containing nanoparticles.

3.0. Affinity for the papillary secretions

Given the physico-chemical and optical properties described in Section 2, nanoparticles have great promise in the field of fingermark detection due to their high surface-to-volume ratio, their size-dependent qualities, their optical properties and the fact that they can easily be chemically tuned. If all these elements are considered together, particles with high selectivity and sensitivity towards molecular or biological targets can be obtained. To use nanoparticles as fingermark sensors, one issue still remains to be answered: "how to maximize the affinity of nanoparticles (whatever their nature) towards the secretion residues,"

Indeed, possessing a good "marker" (in terms of luminescence capabilities or solubility) is only half of the work that has to be done. To obtain well-defined ridges and a good contrast between the marks and the support, it is necessary for the markers (i.e., the nanoparticles) to be engineered so that they present a selective affinity for the secretion residue, and, on the contrary, less or no attraction for the underlying surface. On this subject, some nanoparticles

possess a spontaneous affinity for secretion components as a consequence of their nature (e.g., TiO_2 with haemoglobin-containing marks) [203]) or as a consequence of the synthesis protocol (e.g., colloidal gold particles surrounded by negatively-charged citrate ions in aqueous solution [25]). However, most of the time, additional groups or functions (added by the outer-surface functionalization) are necessary for nanoparticles to be able to target latent secretions.

The choice of the added functional groups greatly influences the way nanoparticles behave when approaching the secretion components. To ensure an efficient targeting strategy, it is necessary to: (1) be aware of the molecular composition of the secretion, (2) determine a list of promising targets, and finally (3) engineer nanoparticles with chemical groups or functions that are able to interact with the identified potential targets. In addition to this, the mode of application also plays a crucial role. Indeed, if the nanoparticles are applied in solution, full benefits can be taken from the various physico-chemical and chemical interactions that take place between two chemical entities. On the contrary, the application of nanoparticles as a dry powder is generally not a very specific application mode since these particles are somewhat "forced" to be in contact with the secretions, to which they mechanically stick. This application mode is thus less sensitive compared to chemically-oriented protocols. This explains why traditional powders are generally limited to fresh marks on non-porous surfaces, since dusting porous surfaces may lead to strong background staining. However, the application in solution is much more difficult to develop since a strong and specific affinity for secretions has to be introduced in the nanomaterials (otherwise, no fingermark will be detected or a strong background staining will be obtained).

When looking at the possible interactions that could take place between a nanoparticle and a latent fingermark, three kinds were identified: "electrostatic", "lipophilic" and "chemical". Most of the existing techniques are driven by the first two. The third one is less encountered but may constitute a serious and efficient alternative for future developments. The following sections will describe each mode of interaction more specifically, with illustrated examples for each one. It should be noted that a fourth mode of interaction could have been added, namely, "physical interaction". However, the role played by van der Waals forces only is not evident since, most of the time, they are generally combined with one of the three other interactions cited above. For example, even the dusting of a powder with a brush on a surface bearing fingermarks requires the addition of lipid or lipid-like material (e.g., stearic acid, other long chain fatty acids, mineral oil, or rosin) to coat the microparticles so they can attach better to the papillary secretions. The use of uncoated particles is only of early historical value. For this reason, we decided not to include this fourth interaction mode, but it will be addressed in the lipophilic interaction section.

3.1. A glance on the composition of secretion residue

The work of Knowles is the most cited reference on this topic [204]. However, Ramotowski's expansion of this work contains more recent information [205]. Basically, under the human skin, there are three types of glands: eccrine and apocrine glands, which produce sweat, and sebaceous glands, which produce sebum. These glands secrete chemicals that help moisturize, lubricate, and protect the skin.

Eccrine glands are found all over the body, but are most concentrated on the palms of the hands and soles of the feet. These areas contain only eccrine glands, which secrete an aqueous

liquid through the pores on the skin. This liquid is over 98% water and contains salt, amino acids, urea, and proteins, and a small amount of lipids, among other chemicals. All are water-soluble except the lipids and proteins, which are dispersed as a colloidal suspension. Per liter, it generates about 0.02 to 0.22 mg of lipids (fatty acids and sterols), 0.3 to 2.59 mg of amino acids, and 150 to 250 mg of proteins [205]. When considering an average molecular weight of proteins between 10,000 to 100,000 g/mole, the concentration of proteins can be estimated between 1.5 and 25.0 nmole/mL. The same calculation can be made for the amino acid fraction, by considering an average molecular weight of 125 g/mole, leading to an amino acid concentration estimated to be between 2.4 and 20.7 nmole/mL. A given volume of eccrine sweat is thus slightly more concentrated (or at least equally concentrated) with proteins than amino acids.

Apocrine glands are mostly found in the arm pits, nipple areola, and genital area. These secrete an aqueous liquid through the base of hair roots. Its composition has not been accurately characterized, but is believed to be low in salt and amino acids and high in proteins.

Sebaceous glands secrete sebum, or what some may call the “fats and oils” of the skin. They are found all over the body, at the exception of the palm and sole area. These glands release their sebum also through the base of the hair root. Although the face and forehead appear to be hairless, they have a high concentration of tiny hair follicles that produce sebum. Sebum consists of lipids and the most commonly found are fatty acids, wax esters (fatty acids esterified with a fatty alcohol), and squalene (levels of squalene are higher in adults than in children).

It is important to note that the secretions on the skin of recently cleaned hands can only come from eccrine glands on the hands. If these hands touch hair or the face, they acquire sebaceous secretions. They can also acquire sebaceous secretions by handling certain food or cosmetic products such as oily foods or hand creams, respectively. Inevitably, this is the case with most fingermarks; it contains both secretions and exogenous contaminants. Furthermore, one normally encounters secretion residue after it has dried. This means that the lipid material, which oxidizes over time, can trap eccrine material. Also, suspended (dispersed) proteins, after they dry, do not easily re-disperse in water (probably due to their aggregation). We shall therefore divide the components of dried fingermark residue into those that are water-soluble or dispersible (salts, amino acids, urea, and any redispersible proteins) and those that are water-insoluble (lipids, non- or low-dispersible proteins, and any trapped eccrine material). The silver physical developer (Ag-PD) is a good example of a technique whose aim is to visualize the water-insoluble components of latent fingermark residue on porous surfaces. Much of what is discussed in this section is taken from Cantu [206].

3.2. Electrostatic interaction

The electrostatic attraction between charged nanoparticles and secretion components is a mechanism that takes place mostly in aqueous-based techniques, since ionic species can exist in solution. Just as section §2.2.2 addressed aspects of the existence of charge and electrostatic interactions at the surface of nanoparticles, here we address those aspects at the level of the secretion components. This is followed by the description of two techniques that were identified as being mostly driven by electrostatic interactions, i.e. multimetal deposition (§3.2.2) and physical developer (§3.2.3).

3.2.1. General principles – Origin and nature of the charge on secretions

As stated in §3.1, when a finger touches an object it leaves some residue consisting of papillary glandular secretions and possibly exogenous material that may have been on the surface of the finger. This residue contains a multitude of chemicals among which are proteins and amino acids that are trapped in water-insoluble lipids. Recall that a protein is an organic compound made of amino acids arranged in a linear chain. Each protein is characterized by its own sequence of amino acids, among a library of 20 different L-α-amino acids. In solution, a protein does not remain linear since it immediately starts to fold into a unique three-dimensional structure. During the folding process, some part of the amino acid chain will link with other parts of the chain, first locally (this is the secondary structure) then at the scale of the whole polypeptide chain (this is the tertiary structure). The tertiary structure is stabilized by non-local interactions (e.g., hydrophobic core, salt bridges, hydrogen bonds, or covalent disulfide bonds), and gives to a protein its catalytic activity. More importantly, in our case, the three-dimensional configuration causes amino acids with ionisable side chains to be present on the outer surface of a protein, facing the aqueous surrounding and thus stabilizing the protein in solution, while neutral amino acids are tightly kept in the hydrophobic core. Among the 20 different amino acids, only a few contain ionizable groups on their side chains: lysine, arginine, and histidine possess basic amino groups; glutamic acid and aspartic acid possess terminal carboxylic acid groups. In addition to this, one has to consider the amino- and carboxyl– ending groups of a polypeptide chain or of each free amino acid. As a consequence, these groups may bear a charge (positive or negative) when they are in contact with an aqueous medium.

When the substrate bearing a fingermark is immersed in an aqueous solution, these chemicals (i.e., proteins and trapped amino acids) are no longer solubilised if they are trapped in the dried, hardened residue. Proteins also do not solubilise (i.e., disperse) well in water. The ionisable groups, in contact with the aqueous surrounding, will thus potentially bear an electronic charge according to their pKa values (the negative log of the acid dissociation constant) and the pH value [207]. Before considering the behavior of the secretion residue as a whole, it is necessary to decompose the system according to the main ionisable functions in presence. In this context, we can distinguish two distinct ranges of pH corresponding to the appearance or disappearance of charges on the functional groups of amino acids (and, by the same way, on proteins through ionization of the external ionisable side chains).

- In the pH range "2-4", negative charges appear (or disappear) if the pH rises (or decreases) from these values. These negative charges find their origin in the deprotonation of carboxyl groups (R-COOH) that are converted to carboxylate anions ($R\text{-}COO^-$). At pH ~2 and above, terminal carboxyl groups are predominantly deprotonated (the terminal carboxyl groups are the ones located at the extremity of a protein backbone or at one end of an amino acid), whereas the carboxyl groups of glutamic and aspartic acids (sidechains) are converted to carboxylate anions at slightly higher pH (~4). See the behavior of “Glu” and “Asp” and also of “Terminal” carbonyl group in Figure 10.
- In the pH range "9-10", positive charges appear (or disappear) if the pH decreases (or rises) from these values. These positive charges find their origin in the protonation of amino groups ($R\text{-}NH_2$) to form ammonium groups ($R\text{-}NH_3^+$). At pH ~9 and below, terminal amino groups are predominantly under the form of ammonium groups (the terminal ammonium groups are the ones located at the extremity of a protein backbone or at one end of an amino acid),

whereas the basic groups of arginine, lysine, and histidine get deprotonated at pH > 10. See the behavior of “Arg”, “Lys” and “His” and also of “Terminal”amino groups in Figure 10.

If the pH of a solution increases, starting from highly acidic values, the positive charge of proteins and amino acids (due to protonated basic groups) progressively decreases (due to the appearance of negative charges from the carboxylate anions), up to reach a "no net charge" point (equilibrium between positive and negative charges), before it becomes negative (due to the deprotonation of basic groups, only the carboxylate anions remain). The "isoelectric point" (pI) is defined as the pH at which a protein has no net charge (considering the individual charges of all the amino acids that comprise it). At its pI, an amino acid is a neutral zwitterion. In other words, it bears simultaneously a negative charge (from its terminal $-COO^-$) and a positive charge (from its terminal $-NH_3^+$). When the pH > pI, a protein bears a net negative charge and when the pH < pI, a protein bears a net positive charge. The pI value also varies between proteins.

The protonation and deprotonation of proteins and amino acids certainly constitute the major contribution to the net charge of the fingermark residue, which varies according to the pH. It should be noted that lipids bearing carbon-carbon double bonds may behave as nucleophiles (Lewis bases) in polar reactions by donating a pair of electrons to an electrophile (Lewis acid) under low pH conditions. It may thus be supposed that positively-charged protons or silver ions can be electrostatically attracted to the electron-rich double bond from mono- to poly-unsaturated fatty acids [40].

Considering all these observations, it is possible to define three pH ranges, in relation with the charge of the residue as a whole (Figure 10):

a. The first pH range (pH ~2-3 and below) corresponds to positively-charged fingermark residue. At these pH values, the amino groups are protonated ($–NH_3^+$), as well as the carboxylic acids (non-charged, -COOH; see grey region in the upper right of Figure 10).

b. The second pH range (intermediate pH value) corresponds to fingermark residue having the least charge. At these pH values, proteins and free amino acids are close to their isoelectric points. Since the residue contains several amino acids and proteins, not all are neutral at the same pH, thus we speak of a range in which the residue has the least charge.

c. The third pH range (pH ~9 and more) corresponds to negatively-charged fingermark residue. At these pH values, the carboxyl groups are deprotonated ($–COO^–$), as well as the amino groups (non-charged, $-NH_2$; see grey region in the lower left of Figure 10).

If one plans to develop a technique based on the electrostatic attraction between nanoparticles and latent secretions, one should set the pH within the first pH range (the acidic one) if the nanoparticles are negatively-charged, and within the third pH range (the basic one) if the nanoparticles are positively-charged. However, since the charge of the nanoparticles is also function of the pH values and could be neutralized if the pH reaches a certain value, it is sometimes necessary to set the pH in the intermediate pH range (the second one), until the Coulombic attraction between the latent mark and the charged nanoparticles is a maximum. To confirm this theory, we will now look more closely at two existing methods, based on negatively-charged nanoparticles in aqueous solution.

3.2.2. Electric charge aspects of the gold sol (description of the MMD in terms of zeta potential, size, and charge)

In multimetal deposition, the colloidal gold solution must be set at a pH between 2.5 and 2.8 for the gold colloidal particles to attach to the latent fingermark residue [25]. Outside this range, the successful detection of latent fingermarks decreases drastically. The explanation for this may lie in the negatively-charged citrate-capped gold particles that are used to detect fingermarks in the first step of this process.

Following the MMD-II protocol [25], the colloidal gold obtained consists of an aqueous monodisperse suspension of 14 nm (diameter) gold colloids, capped with citrate ions, and of a pH of ~6.2. In such conditions, the carboxylic acid groups of the citrate ions are mostly deprotonated. The gold nanoparticles are thus highly negatively-charged and repel each other in solution, avoiding aggregation. This explains why such a colloidal solution is stable for months. In the context of a method based on electrostatic interactions, this constitutes ideal conditions for the gold colloids, since their negative charge is almost at its maximum. Nevertheless, at this pH, the secretion residues are the least charged and possess no specific affinity for the gold colloids. This explains why no fingermarks are detected when immersing a sample in a colloidal gold solution (synthesized according to the MMD-II recipe) whose pH has not been modified from its initial value.

The latent fingermarks should be positively-charged to promote electrostatic attraction. As previously said, the latent residue contains water indispersible proteins which become positively-charged in an acidic environment (due to protonation of the amine groups). With the decrease of the gold solution pH, the latent fingermark residue becomes more positively-charged (protonated). However, a drawback occurs at the same time: the gold nanoparticles become less negatively-charged with decreasing pH (due to the protonation of the carboxylate groups of the adsorbed citrate ions). This effect is empirically observed when decreasing the

pH to 1.7 and below. The ruby-red colored gold colloid immediately turns dark purple, with the gold nanoparticles aggregating due to the neutralization of the citrate ions, resulting in an insufficient electrostatic repulsion compared to the van der Waals attraction. Figure 5 illustrates this effect in terms of zeta potential measurements. It is thus inadvisable to set the pH of the colloidal gold solution at a pH of 2 or below in order to maximize the positive charge of the fingermark residue, because it would result in a highly unstable colloidal gold solution and no detection of fingermarks.

To limit this effect, a neutral non-ionic surfactant (i.e., Tween 20) is added to the colloidal gold before reducing the pH [25]. The stability of the sol at low pH is maintained by steric hindrance. However, the charge of the gold colloid is screened by a ligand replacement effect and the steric effect induced by the capping (Figure 5). Stability is thus obtained to the detriment of the negative charge. Nevertheless, this does not solve the problem of citrate neutralization at low pH values, resulting in uncharged gold colloids.

Consequently, it was necessary to find experimental conditions for which: (1) the gold nanoparticles still possess a sufficiently high negative charge, and (2) the fingermark residues are sufficiently positively-charged to attract the nanoparticles. These experimental conditions have been empirically set at a very narrow pH range between 2.5 and 2.8. Figure 11 schematically illustrates this concept.

We can thus conclude that the multimetal deposition method is one based on electrostatic attraction between negatively-charged nanoparticles and positively-charged fingermark residues. However, due to the constraints imposed by the intrinsic nature of both, this process is taking place in non-ideal physico-chemical conditions in terms of charge (the gold

nanoparticles and fingermark residue are not at their maximum charge). It also explains why this technique is so sensitive to pH modifications.

3.2.3. Electrostatic aspects of the silver physical developer

Silver physical development is a process whereby silver ions get reduced to silver metal by a reducing agent present only at a catalytic site. Such nucleating (catalytic) sites include silver, gold, and silver sulfide (either in bulk or as particles). Since silver catalyzes silver physical development, any silver deposited (reduced) on a catalytic site adds to the catalytic activity of this site and more silver is deposited. This explains why the process is referred to as auto-catalytic. The use of the silver physical developer to detect fingermarks on porous surfaces thus consists of depositing silver nanoparticles on the secretion, so that they may constitute catalytic sites for further silver deposition. We now explain how this occurs.

The development of latent fingermarks on porous surfaces with a silver physical developer depends on the spontaneous formation of silver colloidal particles. Indeed, the silver physical developer (or Ag-PD) is an aqueous solution containing silver ions, a reducing agent, and other components, all of which are carefully balanced so that the silver is not reduced by the reducing agent unless a nucleation site is present. These colloidal particles begin as single silver atoms, which grow to form silver nanocrystals with sizes ranging from 1 to 100 nm. Under some circumstances, these nanoparticles get electrostatically attracted to the latent fingermark residue and become nucleating sites for further physical development [40,208]. Here is a summary of the underlying processes driving the attraction of silver nanoparticles for papillary secretions:

a. The water-insoluble components of latent fingermark residue contain lipids (if the fingers touched skin areas bearing sebum or exogenous lipid-bearing material) and a significant amount of non-dispersible proteins (from the eccrine secretions which contain circa 200 mg/L of proteins and just about 0.12 mg/L of lipids [205]). When latent fingermark residue on a surface dries, the proteins do not readily redisperse in water, they remain on the surface.

b. Similar to the colloidal gold treatment (§3.2.2.), it can be assumed that the water-insoluble fraction of latent fingermark residue becomes positive, since the pH of the Ag-PD is acidic (pH evaluated at 1.38) [40]. The Forensic Science Service (FSS) developed test papers for latent fingermark visualizing reagents, including the Ag-PD [209]. The FSS used a solution of ethylenediaminetetraacetate (EDTA) in its sodium salt form (the four carboxylic acid groups are deprotonated) to print a test pattern on paper. In acid solution, EDTA gets protonated (the four carboxylate groups and the two amines as well), making the molecule acquire a positive charge. It also becomes insoluble. This was done to simulate the protonation of the non-dispersible proteins contained in the latent fingermark residue.

c. No matter how stable the Ag-PD is, silver nanoparticles are formed spontaneously in the solution and grow with time. Their *rate of formation* is suppressed by keeping the possibility of silver ions getting reduced close to zero, but still positive. Hence, their formation is suppressed but not stopped. Their *rate of growth* is suppressed by introducing a cationic surfactant in the formulation. Note, the full electrochemical treatment of the Ag-PD and its stabilization is given by Jonker and coworkers [210], Cantu [40], and Cantu and Johnson [208].

d. Spontaneously-formed silver nanoparticles, just like the gold nanoparticles, are capped with citrate ions and are thus negatively-charged. The magnitude of their negative charge increases with their growth. Though the pH of the Ag-PD is 1.38 [40], the citrate ions are not completely neutralized. Each of these negatively-charged nanoparticles electrostatically attracts cationic surfactant molecules and is prone to get encased by them forming a positively-charged micelle. But those near or on the fingermark residue are also electrostatically attracted to the positively-charged residue. There is a point in their growth where the nanoparticles are mostly negative (they begin at zero, reach a maximum negative charge, and then take a turn towards a positive charge). A schematic representation of this is given in Figure 12. If these (mostly negative) nanoparticles are near or on the positive latent fingermark residue, they attach (electrostatically) to the residue; get neutralized (lose their charge); lose their citrate caps (and thus lose any adhered cationic surfactant molecules); and finally become bare nucleating (catalytic) sites for silver physical development. Figure 13 is a scanning electron microscopic (SEM) image of a silver colloidal particle that has grown on fingermark residue on a paper fiber. It began as a small nanoparticle that grew into a colloidal particle several microns in diameter. The multitude of filaments that make up this particle trap light and thus make the particle appear dark rather than silver in color.

e. Latent fingermark residue is more exposed (i.e., it has more of its components exposed over a larger surface area) when it is on a porous surface than if it were on a non-porous surface. Since the exposed surface components carry a charge, it follows that the apparent positive charge of the residue is higher if it resides on porous surfaces than if it sits on non-porous surfaces. This may explain why the Ag-PD develops latent fingermarks on porous surfaces but not if they were on non-porous surfaces. If the negatively-charged nanoparticles were not dynamically changing in size and charge, then they would gradually adhere to the (less

positively-charged) residue in sufficient number to act as nucleating sites. This happens with the colloidal gold system. The gold colloid particles, which do not change in size or charge, can take up to 2 hours to have a perceptible amount adhere to residue on non-porous surfaces.

3.3. Lipophilic interaction

Lipophilic interactions with nanoparticles are mainly confined to the use of powders to detect fingermarks. Nanoparticles functionalized with lipophilic molecules are described in Section 4 [30,211]. This section focuses on powders and starts with a brief comment on traditional micro-sized powders, in particular about the role played by physical interaction and the need for coating molecules. This is followed by the new trend consisting of using nano-sized powders with enhanced lipophilic abilities. Both approaches, traditional and nano-enhanced particles, are compared in the next section.

3.3.1. Traditional fingermark powders

Traditional fingermark powders consist of micron-sized particles, some with nanostructured surfaces [45]. Many of these particles are coated with lipid or lipid-like material (e.g., stearic acid, other long chain fatty acids, or mineral oil) or blended in with lipid-like substances (e.g., starch or rosin/resins) for greater adhesion. But some are raw (“naked”) uncoated particles, particularly those in earlier powders. Coated particles adhere to latent fingermark residue via lipophilic attraction while uncoated ones probably adhere via van der Waals attraction forces (which depend on both the nature of the particle and the residue) provided they are sufficiently near the surface (as when they are applied with a brush). These van der Waals attractive forces can attract (adsorb) atoms, molecules, or ions (as noted in §2.2.1) from the

surroundings. The resulting particle can be charged if it adsorbs ions or remain neutral if it adsorbs neutral species. These capped particles further interact with the residue via van der Waals forces. Furthermore, since the surface roughness of the residue is in the micron range, the nano-sized particles can easily get lodged within the surface roughness.

Traditional fingermark powders are generally applied to non-porous surfaces, especially at crime scenes, to develop latent fingermarks up to months after their deposition if the substrate has been protected from external degradation. But when applied to porous surfaces, they develop marks that are only a few days old since the residue dries more quickly on these surfaces than on non-porous surfaces.

Another way of promoting lipophilic interaction with particles involves putting micron-sized particles in solution, namely those found in small particle reagents (SPRs). Such solutions contain surfactants and work best on wet or dry non-porous surfaces. The original SPR consisted of molybdenum disulfide and the resulting reagent is black. The particle size can be as small as 400 nm. Currently SPRs exist that are white (based on titanium dioxide or zinc carbonate) and/or fluorescent (e.g., made by mixing zinc carbonate and fluorescent dyes).

Therefore, the coating of traditional micro-sized nanoparticles rapidly shows its limits, especially in terms of the age of the fingermarks and the background staining. One way to enhance the ability for powders to more selectively or more efficiently develop latent traces involves enhancing the lipophilic character of the particles to be powdered or applied as SPR. The use of nanoparticles that can be chemically modified offer an important opportunity in this domain. This evolution is described in the following section.

3.3.2. Powders containing enhanced nanopowders

Nano-sized particles can be coated or non-coated; but, they can also be functionalized whereby molecules are chemically bonded to the surface of the nanoparticles. Such chemically-bonded functionalization can also be applied to micron-sized particles, but to our knowledge this has not been reported, particularly for visualizing latent fingermarks. Some powders made with nanoparticles visualize very weak latent fingermarks better than traditional powders do [8]. It should be emphasized that when such small particles are in powder form and become aerosolized, they could be hazardous to one's health as stated in Section §2.5.

3.3.3. Illustrated example – Alkane-modified metal nanoparticles

Functionalized nanoparticles can be obtained through covalent bonding of molecules on their outer surface, as indicated in section §2.4. Groups such as thiol and amine readily bind to the gold surface. Amine groups also bind well covalently on the surface of quantum dots, such as those having a ZnS shell with a CdSe core.

Sametband and coworkers used these properties to develop two types of reagents for visualizing latent traces [30]: gold nanoparticles functionalized with n-alkanethiols and CdSe/ZnS quantum dots coated with n-alkaneamines (Figure 14). How well these reagents visualized latent marks depended on the size of the alkane chain, with a C18 chain working best for both reagents. In any case, the lipophobic interactions are promoted compared to "classical" powders, leading to more detailed fingermarks with less unwanted background

staining, as noticed by Choi and coworkers [211]. These aspects are discussed in greater detail in Section 4.

3.4. Chemical reaction

Some of the most efficient detection techniques are based on chemical reactions between an organic reagent and some components of the latent fingermarks, especially the amino acid-reagents on porous surfaces (e.g., ninhydrin, 1,2-indanedione, or genipin). This mode of interaction can be highly selective (in terms of recognition of chemical groups or patterns) and is also highly effective since chemical bonds are formed between the reagent and the latent secretions. Nevertheless, this third interaction mode is still rarely encountered in the field of nanoparticles, where electrostatic and lipophilic interactions prevail. The pioneering works of Menzel somewhat opened the road to this mode of recognition and may constitute a serious and efficient alternative for future developments [212,213].

3.4.1. General principles

We define a technique as being driven by "chemical reaction" if a covalent bond is actually created between the reagent and the fingermark residue. Only non-covalent interactions led to the detection of fingermarks in the techniques previously described (e.g., physical entrapment in lipids or electrostatic interactions). The formation of a chemical bond requires a molecule or a functional group to be present in most of the latent residues and able to undergo chemical reactions under ambient or mild conditions with other chemical groups. It is not necessary that the chemical reaction lead to some colored or luminescent product (like for amino acid-reagents such as ninhydrin or 1,2-indanedione), since the goal is to form a covalent link

between the particle (the "marker") and the residue. Once this is done, it is supposed that the particle will remain "stuck" to the residue at the location the reaction occurred. The use of dye-doped nanoparticles will permit detection of the nanoparticles and, in the same way, make make the latent fingermark appear.

Two major limitations of this strategy may explain why it has not encountered the success it should meet:

- First, the chemical reaction between the secretions (the target) and the functionalized nanoparticle (the sensor) has to be a fast process. Indeed, it seems useless to propose a fingermark detection technique requiring 24 hours of immersion in order for the chemical reaction to occur. A solution could involve finding a way to speed up the kinetics of the reaction by using a catalyst or by activating one of the two reactive groups (e.g., by forming an unstable intermediate that will readily react with another chemical group) prior to the immersion of the specimen in the working solution. However, it could considerably burden the application protocol and, simultaneously, reduce the forensic scientist’s interest in this technique.

- Second, the chemical groups surrounding the nanoparticles must be specific to latent secretion residue and not to the underlying substrate. Since a major part of the latent residue components are of organic origin, it seems logical to try targeting amino or carboxylic groups that are very likely to be present in almost all latent fingermarks (e.g., in amino acids, proteins, or some lipids). However, since a great part of the substrates may also have an organic origin, they may also constitute targeting sites for the functionalized nanoparticles. In

such a case, an unwanted background staining will occur, reducing the selectivity for fingermarks and the contrast.

3.4.2. Illustrated example – Amide bond formation

Fingermark residue contains several chemicals, each of which has at least one carboxyl group. These include amino acids, fatty acids, and proteins. Menzel felt these molecules could be visualized by chemically reacting them with molecules containing amine groups at one end and a luminescent nanoparticle at the other [214]. Indeed, an amine can react with a carboxyl group to form a very strong amide (peptide) bond (Figure 15).

The reaction is referred to as dehydration synthesis or condensation. The bond C(=O)–NH is called an amide (peptide) bond, the group –(C=O)–NH– is called an amide group or peptide group (when in proteins), and the molecule R–(C=O)–NH–R’ is called an amide. Here the –NH group is a secondary amine.

The molecules with amine groups at one end and a quantum dot at the other that Menzel considered are Cd-based quantum dots functionalized with polyamidoamine (PAMAM) dendrimers. These dendrimers (tree-like structures) have amines at one end and amines covalently bonded with the quantum dot at the other. This approach is described in greater detail in section 4.2.

4.0. Visualizing fingermarks using nanoparticles

Techniques that are based on the use of nanoparticles were first proposed in the 1970s, with the introduction of the silver physical developer by the Atomic Weapons Research Establishment (AWRE) [215,216]. Nevertheless, most of the efforts to take full advantage of nanoparticles, in terms of optical properties and surface engineering, only started in late 1990s and increased very rapidly since 2004. As an illustration of this increased interest, it can be observed that the number of publications related with the use of nanoparticles to detect fingermarks was of only 1 for the 2001-2004 year range (source: Interpol report) [217], 10 for 2004-2007 [218], and 27 for 2007-2010 [219]. The decision has been made to organize the following overview according to the chemical nature of the nanoparticles. Some kinds of nanoparticles have been obviously attracting more interest from researchers (i.e., gold- and cadmium-based nanoparticles) compared to others. Some other domains have also emerged and will certainly soon constitute highly promising alternatives to existing techniques (e.g., silica-based nanoparticles).

4.1. Aluminium-based nanoparticles

Sodhi and Kaur chose to coat aluminium oxide nanoparticles with two different molecules: Eosin Y (a fluorescent dye) and a natural hydrophobic substance [220]. Their aim was to obtain a "nanopowder" to be dusted on substrates and characterized by an enhanced ability to detect fingermarks through lipophilic interactions. According to the authors, this nanopowder detects fingermarks on a wide range of surfaces such as porous and non-porous, as well as white and multicolored ones. It is particularly suitable for detecting fingermarks on glossy items, or on moist and sticky surfaces. The developed marks are luminescent (yellow-green color) when illuminated at 550 nm.

4.2. Cadmium-based nanoparticles

Cadmium is the most commonly used element to synthesize highly luminescent quantum dots (QDs), with numerous publications about their synthesis (see §2.1.2). This explains why the forensic use of QDs to detect fingermarks is limited to the use of cadmium sulphide (CdS) [42,213,214,221-225], cadmium selenide (CdSe) with or without a shell [30,43,212,226], and cadmium telluride (CdTe) [41,227,228]. All these nanocrystals were chosen for their remarkably high luminescent properties combined with the possibility of being chemically functionalzed. Two trends are observed when considering QDs in the detection of fingermarks: those incorporating the nanocrystals in a more massive and bulky structure (typically a polymer) taking benefit only from the luminescence of the QDs [42,212,214,222,224,225], and those considering the nanocrystals not only as fluorescent markers, but especially as probes able to target latent residue by themselves [30,41,43,221,226-228]. In this latter case, a surface modification of the nanocrystals, using self-assembled monolayers of linear molecules, may be necessary.

Menzel and coworkers performed the pioneering work on the use of fluorescent semiconductor nanocrystals as fingermark labelling agents. Their first attempt consisted of solubilizing CdS nanocrytals capped with dioctyl sulfosuccinate (a two-branched molecule that exposed its aliphatic chains to the surroundings of the particle) in heptane or hexane (Figure 16) [221]. Such nanoparticles were applied on cyanoacrylate-fumed, and unfumed, fingermarks on aluminium and metallic soft-drink cans, as well as on the sticky-side of unfumed adhesive tapes. The choice for QDs emerged from the desire to use phase-resolved detection to reduce the unwanted background fluorescence, since QDs are characterized by longer luminescence lifetimes than that of the background [212]. The application protocol

consisted of immersing the substrates (previously fumed or not) for a few seconds to a few minutes in the nanocrystal solutions before rinsing them with an organic solvent. Examination using an argon-ion laser operating in the near-UV allowed for the observation of intensely fluorescent fingermarks on the cyanoacrylate-fumed aluminium and metallic soft-drink cans (Figure 16). Unfumed fingermarks on metal, glass and plastics could not be developed by following this procedure, certainly due to a degradation of the latent marks caused by the organic solvents. On the sticky-side of unfumed adhesive tapes, the results were limited but encouraging, especially on black electrical tape.

Another attempt involved functionalizing CdSe/ZnS QDs with carboxylate groups to form amide bonds with amino acids in the secretions [212]. The detection of fingermarks on aluminium foil required an immersion time of 24 hours, much too long for operational use. According to the authors, no ridge detail could be observed if unmodified QDs were used.

Recently, Gao and coworkers propose to functionalize CdTe QDs with ionisable groups allowing them to obtain negatively-charged QDs (i.e., $-COO^-$) or positively-charged ones (i.e., $-COONH_3\text{-}NH_3^+$), upon modification of the pH of the solution by using hydrazine ($NH_2\text{-}NH_2$) [228]. The detection protocol consisted in setting the pH of the QD solution between 7 and 11, pouring 1 mL of the solution on the latent fingermarks, allowing it to react for 30 min to 1 hour, and then rinsing with water. The authors explain that the detection mechanism is based on the electrostatic interaction between the charged QDs and the amino acids from the secretion, at pH > 6.4, with an increased efficiency for positively-charged QDs. However, a closer look of the illustrated fingermarks makes it clear that several of those fingermarks are "reversed" (meaning that the substrate has reacted, not the ridges). This point has not been raised by the authors, nor discussed. Several explanations may explain this: (1) contrary to

what the authors claim, the amino acids are not sufficiently negatively-charged at pH ca. 6.4 (as illustrated in Figure 10), (2) when the pH is sufficiently high for amino acids to be negatively-charged (near pH 9), hydrazine is expected to be under its basic, uncharged form (since its pKa is 8.1), and by the same way the QDs too, (3) the formation of "-$COONH_3$-NH_3^+" groups is quite hard to understand from a chemical point of view since it stands on the double protonation of the hydrazine molecule. This attempt to develop an electrostatic-attraction-based method is interesting, but it is more likely to believe that the detection is lead by other mechanisms, particularly an unwanted deposition of the QD on the substrates.

In further experiments, efforts were concentrated on the in situ synthesis of QDs inside a polyamidoamine (PAMAM) dendrimer solubilized in methanol or in 1:9 methanol:water and used as cyanoacrylate staining dyes [42,212,214,222]. According to Menzel, the number of functional groups on the surface of the dendrimers (i.e., amino or carboxylate groups, depending on the kind of dendrimer that was used) may play a key role in the solubility of the reagent, in the interactions with latent secretions (physically and chemically), as well as in the reduction of unwanted background staining. Fresh fingermarks on aluminium foil and polyethylene bags were fumed and then immersed overnight in the nanocomposite solution before being observed for luminescence. It remained somewhat unclear to the authors whether or not the staining was due to physical interaction or chemical reaction (i.e., through the formation of actual peptidic bonds between the amino groups of the dendrimer and the carboxylic acids from the secretions). Further experiments were conducted to answer this question. First, fingermarks were "activated" by pre-treating them in a 2.5% (w/v) diimide aqueous solution for 5 to 24 hours at room temperature (shorter immersion times led to no observable fingermarks) before dipping them overnight in the amino-based nanocomposites [212,213]. A second attempt consisted of mixing stoichiometric amounts of diimide with

carboxylate-based dendrimers (without QDs) to pre-activate them. The 1:9 methanol:water mixture containing the dendrimers was left overnight at 60°C. After this step, QDs were added and the fingermarks were finally immersed in the final mixture. Diimide compounds are known to activate the carboxylate groups to increase their reactivity towards amino groups. During their two experiments, Menzel and coworkers tried to promote the formation of peptide bonds between the nanocomposites and fingermarks by either activating the carboxylate groups contained in the latent secretions (first experiment) or by activating carboxylate-based dendrimers that could further react with amino groups contained in the latent secretions (second experiment). The formation of the CdS/dendrimer nanocomposite followed by diimide addition (prior to fingermark treatment) was not successful. Development attempts on porous surfaces were unsuccessful due to unwanted background staining.

Dilag and coworkers used CdS quantum dots, with an average size of ~6 nm, entrapped in chitosan (a biopolymer), leading to nanocomposites of ~20 nm of diameter [223]. The nanocomposites were freeze-dried and applied as a powder with a brush on both cyanoacrylate-fumed and unfumed fingermarks on aluminium foil. Successful results were obtained only when dusting unfumed fingermarks. The nanocomposites deposited on the secretions and permitted the visualization of ridges in the luminescent mode. When evaluating the performance of their nanocomposites, the authors admitted that conventional micron-sized powders gave finer results compared to theirs, explaining that the freeze-drying process certainly led to the formation of large aggregates, with a size greater than those contained in classical powdesr (~1-10 microns).

Sametband and coworkers synthesized core/shell CdSe/ZnS QDs with average size of ~3 nm and functionalized them with octadecaneamine (Figure 14). The nanocomposites were solubilized in petroleum ether to detect untreated latent fingermarks on silicon wafers and paper strips [30]. Their strategy was based on the liphophilic interactions that could take place between the n-alkane ligands covering the QD surface and the lipids from the latent mark secretions. Fluorescent fingermarks could be visualized immediately on the silicon wafers, when illuminated with UV radiation. However, it was impossible to observe fingermarks on the paper strips, due to a strong background luminescence caused by an unwanted deposition of QDs on the porous substrate itself. Further developments are thus required.

More recently, publications referred to the use of thioglycolic acid-stabilized QDs suspended in water to detect latent fingermarks [41,43,226,227]. Thioglycolic acid (TGA) is a small molecule bearing a thiol group on one of its extremities, which allows its binding on the QD surface, and a carboxylic group on the other side, which allows its solubilization in aqueous solution. Wang and coworkers proposed the use of TGA-capped CdSe nanoparticles in aqueous solution to develop fingermarks on the sticky side of adhesives [43,226]. Sebaceous fingermarks were deposited on different kinds of colored adhesives, and immersed in a basic solution of QDs for 15 minutes (pH 8-11). Clearly-defined ridges were observed (Figure 17). The same strategy has been followed by Liu and coworkers, who used TGA-capped CdTe quantum dots to detect latent fingermarks on non-porous substrates [227]. Becue and coworkers proposed the use of CdTe nanoparticles in aqueous solution to detect bloody fingermarks on different non-porous surfaces [41]. The procedure consisted of immersing the substrates in an acidic solution of QDs (pH 3.5) for ~20 min. When comparing their results with those obtained using a conventional luminescent blood reagent (i.e., Acid Yellow 7), they concluded that QDs were equally sensitive on glass, polypropylene and polyethylene

sheets, but far more sensitive on aluminium foil, compared to Acid Yellow 7 (Figure 18). They additionally observed the fact that non-blood latent fingermarks (fresh sebaceous ones) were successfully detected by following the same procedure.

4.3. Europium-based nanoparticles

In the early 1990s, some authors reported the use of europium for the detection of fingermarks as a post-ninhydrin reagent [229], as a cyanoacrylate stain [230-233], or as a lipid-reagent on untreated fingermarks [234-237]. One of the great advantages of using rare-earth elements, like europium, resides in the narrow emission band (~10 nm) located in the red region of the visible spectrum. Such a narrow band permits an efficient and precise filtering of unwanted backgrounds (especially when samples are excited with UV radiation). Moreover, europium is also characterized by a long excited-state lifetime compared to classical fluorophores, especially when it is chelated by organic ligands. The above-cited authors generally used chelating agents and detergent molecules to form a bulky structure around the europium ions, isolating them from the surrounding solvent molecules (e.g., water) [236]. Even if such structures do not fit exactly the definition of "nanoparticles" or "nanocomposites" in the way we defined them at the beginning of this section, the principle remains the same as if one would like to entrap europium ions into silicate nanospheres (See §4.6).

More recently, Menzel and coworkers used europium oxide (Eu_2O_3) nanoparticles to detect fingermarks [238]. Contrary to the above-cited works, actual Eu_2O_3 nanoparticles were amino-functionalized to target carboxylic acid groups contained in the latent secretions (Figure 19). Experimentally, the procedure required the immersion of the specimen in an aqueous solution containing the reactive compounds and heating it to 70- 80°C for 30 min for

optimal results. Without heating, no development was observed. It has to be noted that very fresh fingermarks (5 hours) gave good results, whereas one-week-old marks gave poor ridge details.

4.4. Gold-based nanoparticles

One of the most common applications of gold nanoparticles in aqueous solution for the detection of latent fingermarks is certainly the multimetal deposition technique (MMD). Briefly, this technique is a two-step, wet chemical process consisting of the deposition of gold nanoparticles onto the latent residue under acidic conditions (pH 2.5-2.8), followed by an enhancement step to allow the visualization of the gold nanoparticles through an increase in their size (Figure 20).

Initially developed by Saunders [239], the method has further been improved by Schnetz and Margot [25], who modified the procedure to increase the reproducibility of the results and the stability of the solutions. They also concluded that gold nanoparticles with a diameter of 14 nm were best suited for this method. This improved formulation is nowadays known as the "MMD-II" method and its effectiveness compared to the original formulation has been confirmed by Jones [240]. In 2006, Choi and co-workers observed marks treated with MMD-II using a scanning electron microscope and confirmed the observations made by Schnetz [241], who visualized the gold nanoparticles on the secretions and their absence in the inter-ridge region. Recently, Zhang and coworkers showed that it was possible to chemically image MMD-enhanced fingermarks using a scanning electrochemical microscope (SECM) [242]. The principle of this method lies in the possibility of measuring the redox activity of a localized area due to the solubilization of the deposited silver. Since silver is preferentially

reduced on the gold nanoparticles, which are themselves located on papillary ridges, it was possible to visualize the ridge details by scanning fingermarks detected by following the MMD protocol. This method could help visualizing classical MMD results on dark or patterned substrates. However, it needs to be optimized to enlarge the scanning area and to reduce the time required to perform a scan before it could be applied in practice.

The biggest advantage of MMD lies in its relative efficiency on various kinds of substrates (porous, non-porous, and "difficult" ones like polystyrene or Euro banknotes), as well as its ability to detect fresh as well as aged fingermarks, even if those have been previously wet. However, the technique is not routinely applied, mainly because it is labor intensive (several baths, long immersion times) and because the quality of the results are highly sensitive to pH variations during the gold nanoparticles deposition. Indeed, a non-ionic surfactant is required to stabilize the colloids in solution and the pH of the working solution has to be maintained between 2.5 and 3.0 during the deposition step. This is necessary for the gold colloidal particles to be attracted by the secretions (see §3.2.2). If those conditions are not met, gold nanoparticles do not ideally deposit well on the secretions. The resulting contrast will be poor or negative. This gold deposition step is thus crucial but the user has limited influence on it. For example, once immersed, some papers may induce a strong modification of the pH leading to no result at the end. Moreover, gold nanoparticles surrounded by silver appear as dark brown fingermarks, which is not ideal when dealing with dark or complex, multi-colored printed substrates.

Further developments have been made to improve the initial MMD-II method. One attempt consisted of taking advantage of the ability for gold nanoparticles to be functionalized by thiolated molecules. Becue and co-workers proposed a "one-bath" alternative for MMD by

functionalizing the gold nanoparticles with thiolated cyclodextrins (doughnut-shaped molecular hosts) bearing a dye. The results were encouraging [26], but the technique was not ready for application to casework. Indeed, long and complicated synthetic steps (synthesis of the modified cyclodextrins, followed by colloidal gold modifications) were required before obtaining the working solution. Another attempt involved modifying the enhancement step. This step initially consisted of depositing silver onto the gold nanoparticles to allow their visualization [25]. Stauffer and coworkers replaced the silver-on-gold enhancement by a gold-on-gold treatment, using gold chloride and hydroxylamine [27,28]. This alternative to MMD-II was called "Single Metal Deposition" (SMD), since only gold is used to detect fingermarks. According to the authors, SMD represents an advantageous alternative to MMD mainly due to lower costs, fewer solutions to prepare, and a shorter procedure since one bath has been removed. Finally, one of the latest evolutions of the method has involved obtaining luminescent fingermarks by replacing the silver (or gold) enhancement step by the formation of a ZnO shell around the gold nanoparticles [243]. The advantages that are offered by this modification are the use of the MMD method on black or complex, multi-colored printed substrates, thanks to observation in the luminescence mode (Figure 21-a). Moreover, ZnO nanoparticles are able to emit in the UV-range, allowing the visualization of fingermarks on substrates that may present strong background fluorescence in the visible range, like illustrated in Figure 21-b.

Recently, an original approach was proposed to enhance the selective binding of gold nanoparticles with the secretion residue as a pre-step to an MMD/SMD process [244]. As said before, the covalent binding of thiolated molecules with the surface of gold nanoparticles occurs spontaneously at room temperature. A way to exploit this affinity is proposed by Almog and Glasner who described a two-step process. First, a ninhydrin analogue bearing a

thiol function (i.e., a thiohemiketal - THK) is used to detect fingermarks by reacting it with the amino acid fraction of the residue. This makes the fingermark visible by the formation of Ruhemann's purple, but it also locally enriches the secretions with insoluble long-chained aliphatic thiols, which are byproducts of the reaction of THK with amino acids. The second step consists in processing the enriched fingermark with an MMD/SMD process. Gold nanoparticles are consequently expected to deposit more likely on the ridges due to the formation of thiol-gold bonds. The published article refers only to the synthesis and use of THK as amino acid reagent leading to the successful formation of Ruhemann's purple [244]. Another article is expected describing the second step, involving gold nanoparticles.

Gao and coworkers proposed a one step MMD-like process to detect fingermarks, using glucose-capped gold nanoparticles and operating in a wider range of pH [245]. On the contrary to what the authors claim, the mechanism looks more like a “gold-based SPR”, especially when it is said that it is working with blueish colloidal solution (this color being a consequence of nanoparticles aggregation). Another one-step "MMD-like" process was proposed based on the *in situ* reduction of tetrachloroauric acid (HAuCl4) into visible gold nanoparticles by the secretion themselves [246]. The authors identified lecithin as one of the secretion components able to reduce the auric salt into gold nanoparticles, resulting in pink/purple fingermarks. Personal attempts to reproduce the published results failed and further investigations are consequently required to assess the actual efficiency of this technique.

Besides MMD, other methods use gold nanoparticles as intermediates for the detection of fingermarks in solution. Sametband and coworkers synthesized gold nanoparticles functionalized by n-alkanethiol (Figure 22), and solubilized them in petroleum ether [30]. The

alkanethiol ligands strongly bind to the gold nanoparticle through covalent bonds with the thiol group, leaving the aliphatic chain in contact with the surrounding solvent. The authors took advantage of the lipophilic interactions between the aliphatic chains and the fatty acids from the latent secretions. After an immersion time of ~3 minutes in the gold nanocomposites solutions, a silver physical developer (Ag-PD) was subsequently applied to allow the visualization of ridges as dark impressions. According to the authors, the hydrophobic capped gold nanoparticles improve the intensity and clarity of the developed marks compared to Ag-PD alone (Figure 22). Moreover, they found a relation between the chain length and the quality of the developed fingermarks, the results being better when using longer alkanes. This observation confirmed the role played by lipophilic interactions in the deposition process.

Leggett et al. presented a way to detect specific drug metabolites in secretion residue, to provide evidence of drug use (and not only by touching contaminated objects) [156]. Briefly, cotinine (a metabolite of nicotine present in the sweat of tobacco smokerers) is targeted with anti-cotinine antibodies bound to gold nanoparticles and combined with a fluorescent marker. Highly detailed fingermarks, with 3rd level minutiae were obtained on glass slides (Figure 23). In this case, gold nanoparticles play the role of antibody carrier and signal enhancer (given that approximately 50–60 antibody molecules may be bound to each nanoparticle).

Another trend related to the use of gold nanoparticles consists of developing new dusting powders (not to be used in solution) based on gold nanoparticles to which aliphatic chains are attached. Choi and coworkers coated gold (and silver) nanoparticles with oleylamine, a long-chain lipophilic molecule, so that the obtained nanopowders would preferentially be deposited on the lipid-containing components of the latent fingermarks (Figure 24) [211]. All of the nanopowders produced at least satisfactory performance on glass and painted wood, but the

fingermarks on the plastic and aluminium surfaces were more difficult to develop, especially when they were not fresh. When compared with conventional micron-sized ones, the gold-based nanopowders produced sharper and clearer development of the latent fingermarks, without background staining, even if less contrast was generally observed compared to black classical powders (Figure 24). By comparison, classic (magnetic) powders are composed of flakes ranging from 5 to 25 μm in diameter [247,248], which is 500 to 2500 times larger than functionalized nanoparticles. Additionally, the authors successfully enhanced ridge detail by following the procedure with a silver physical developer.

4.5. Iron-based nanoparticles

Iron oxide (Fe_3O_4) powder is of a particular interest to detect fingermarks due to its intense black color. Since it is possible to obtain nano-sized iron oxide particles, it is worth citing its conventional use as suspended particles to detect latent fingermarks on non-porous surfaces [249] or, more recently, on the adhesive side of white or light-colored tapes [250]. Iron oxide constitutes a really good alternative to conventional small particle reagents (SPR) and it produced better sensitivity, ridge detail and contrast.

Magnetic iron oxide nanoparticles were also used in an antibody-directed approach to detect a range of drugs (e.g., THC from marijuana and methadone) or drug metabolites (of methadone and cocaine) contained in the fingermarks, either through consumption or manipulation [158-162]. This approach is similar to Legget's, who targeted cotinine using anticotinine-functionalized gold nanoparticles [156], with the additional advantage offered by the magnetic core which facilitates the removal of unbound particles using a magnetic wand. The remaining nanoparticles (bound to the fingermarks) were fluorescently tagged before

observation. Positive results were obtained for the drugs and metabolites tested, with visible third level details such as pores.

4.6. Silica-based nanoparticles

Silica-based nanoparticles are initially non-luminescent, but they can be doped with organic dyes or rare-earth compounds to become extremely luminescent species (see §2.3.3). When used in biological imaging applications, uncoated silica nanoparticles suffer from a number of disadvantages, such as nonspecific adsorption of proteins [251]. Such phenomena could be an advantage in the case of fingermark detection since the secretion residue contains proteins. Despite this fact, the use of luminescent silica nanoparticles in forensic science still remains rare. Theaker and coworkers recently chose to enclose a variety of colored and fluorescent molecules (i.e., fluorescein, thiazole orange, oxazine perchlorate, methylene blue, Basic Yellow 40, Basic Red 28, rhodamine B, and rhodamine 6G) into silicate particles [44]. The resulting doped nanoparticles were used as aqueous suspensions to detect fingermarks. Micron-sized particles were also used as dusting agents. Both fresh (20 min) and aged fingermarks (40 days-old) presented good definition after development (Figure 25). Similarly, Chen and coworkers modified the surface of dye-doped clay with phenyltriethoxysilane, before grinding the material with a mortar and pestle [252]. The fluorescent powder obtained was used to detect very fresh fingermarks (few minutes) on glass. According to the authors, using amino-functional silanes instead of using dyed clay without surface modification does not give good results. Nevertheless, in this example, microparticles are likely to have been obtained instead of nanoparticles. Finally, functionalized silica nanoparticles were also used to help determining the molecular composition of fingermarks [253]. For this study, positively-charged silica nanoparticles and hydrophobic ones were used to separate the polar

components (i.e., amino acids) and non-polar ones (i.e., squalene and fatty acid), respectively, of secretion residue left on a glass slide.

4.7. Silver-based nanoparticles

The physical developer (PD) is certainly the best known technique based on the use of silver nanoparticles, which currently constitutes the reagent of choice to visualize the water-insoluble components of latent fingermark residue on porous surfaces. One of its latest formulations has been given in the chapter written by Ramotowski in this book. The diagram below summarizes the procedure used for visualizing latent fingermarks on paper using the Ag-PD (Figure 26).

Historically, physical developer was first developed for photographic purposes. It thus had no initial link with the detection of latent fingermarks, mainly due to the fact that the existing formulations were highly unstable. Some enhancements were proposed to extend the stability of the solution by a few hours [254]. But the seminal work of Jonker and coworkers [210] from the Philips Research Laboratory (Einhoven, The Netherlands) can somehow be identified as the actual start of this technique with a formulation of a highly stable silver physical developer, which they referred to as FC1 (F for the ferrous/ferric redox couple and C for citric acid). Their application was not for use in classical photography, but for the photofabrication of printed circuit boards. Shortly after their formulation was published, scientists in the United Kingdom (UK) became aware of its use for visualizing latent fingermarks on porous surfaces. This formulation was further called "Philips physical developer" by researchers involved in its use in forensic science [255]. An excellent history of how the U.K. studied, modified, and implemented the use of the Ag-PD for visualizing latent

fingermarks is given by Goode and Morris [216]. Cantu and Johnson also summarized the historical development in their chapters on silver physical development [40,208]. Several modifications were made and eventually a recommended formulation was provided for use by police laboratories in the U.K. A major one by the Police Scientific Development Branch (Sandridge, U.K.) was the replacement of distilled water by the more pure reverse osmosis/deionized (RO/DI) water, which, in doing so, prompted a reduction of the amount surfactants used. Burow discusses this change [256]. Since then other modifications have been made, one of which was the change of the surfactant Synperonic N to Tween 20 due to the possible phasing out of the former [257]. Interestingly, this surfactant substitution gives greater stability to the Ag-PD [258].

If a silver or silver oxide fingermark is weak or if it has an interfering background, several methods exist to enhance such a mark, independently from the formulation that is used [40,208]. Three of them are detailed:

- A mild hypochlorite solution (e.g., a dilute solution of household chlorine bleach) can be used to darken the fingermark and bleach the paper, resulting in an increase of the general contrast. The darkening of the fingermark is due to the reaction of hypochlorite ions with silver to form dark brown silver oxide.

- Another post treatment involves using a reagent involving potassium iodide (KI). Initially developed by Dr. G. Saunders, this post-treatment has been detailed by Cantu and coworkers [259]. Briefly, a silver or silver oxide fingermark is converted to whitish-yellow silver iodide fingermark due to the reaction between silver (or silver oxide) and the KI-based reagent. At the same time, the paper turns dark brown to black due to the reaction between tri-iodide ions

in the KI-based reagent and starch, which is most current paper contain. Figure 27 is an example of how this method enhanced a PD fingermark on a counterfeit banknote.

- A third post-treatment involves transferring a silver or silver oxide fingermark onto a specially treated paper or film. The underlying idea is to transfer only the mark (not the background) onto such a white or clear surface. This treatment is actually based on a physical development process, requiring three things: (a) a brominating (bleaching) solution that converts the silver or silver oxide fingermark to a silver bromide fingermark; (b) a solution containing sodium thiosulfate (“hypo”), which converts the silver bromide to a soluble silver thiosulfate salt, and a photographic chemical developer; and (c) a gelatin-coated paper or film impregnated with colloidal gold particles, onto which the silver thiosulfate ions are reduced to silver by the chemical developer. This method is briefly described by Cantu and Johnson [208] and extensively treated by Land [260] and Levenson [261].

As a final comment, contrary to gold nanoparticles, not much work has been done in creating new detection techniques based on (functionalized) silver nanoparticles. We can however cite the work performed by Choi and coworkers, who functionalized silver nanoparticles with oleylamine, a long-chained lipophilic molecule [211], as described in the section dedicated to gold-based nanoparticles. However, the contrast that was obtained using silver-based nanopowder was less than the one obtained using gold-based nanopowder. For this reason, and due to a heavier and more time-consuming synthetic procedure, the use of silver-coated nanoparticles was not pursued.

4.8. Titanium-based nanoparticles

Titanium dioxide (TiO_2) is a well-known semi-conductor material extensively used in optical, electrical and photo-catalytic applications starting from the second half of the twentieth century. TiO_2 has been used to detect latent fingermarks, mainly on non-porous substrates, as a powder or suspension. Some authors also report its use to detect blood marks, discussed below. Commercially available TiO_2 particles are generally of a range of sizes near the sub-micron (0.2 to 0.3 microns, corresponding to 200 to 300 nm).

Due to its white color, its high refraction index and its lack of absorption in the visible range of light, TiO_2 is extensively used as a white contrasting agent that can be useful on dark or transparent substrates. Given its extremely low solubility in water and organic solvents, the classical application modes that prevail are dusting powders, white small particle reagent solutions (SPR-w), and paste-like formulations (white powder suspension - WPS). Micron-sized TiO_2 particles constitute a good alternative to zinc carbonate for the preparation of SPR-w to be used on non-porous surfaces or on the adhesive-side of dark or transparent tapes, with excellent results obtained on such substrates [262-264]. Similarly, SPR-w can help in detecting fingermarks on substrates that were previously wet [265]. An experiment carried out on immersed plastic (vinyl acetate), glass and painted metal surfaces (up to one month), showed no influence of the immersion time and of the substrate's nature in the quality of the results [266]. According to the authors, only the way the surface has been touched and the duration of contact played a role. Finally, TiO_2 is currently recommended by the Home Office (HOSDB, UK) to be used in their white powder suspension (WPS) formulation to detect fingermarks on the adhesive side of black or dark tapes, and it replaces the classical sticky-side powder™ (SSP) [250].

Another field of application of TiO_2 is the detection of latent blood fingermarks on non-porous and semi-porous surfaces, when suspended in anhydrous methanol [203]. The application protocol involved spraying the methanol-based suspension (1 g TiO_2 in 10 ml methanol) onto the surface of interest, then rinsing it with pure anhydrous methanol. The results were excellent on non-porous surfaces, with fingermarks appearing in white and presenting 3rd-level details. Bergeron observed no difference between fresh fingermarks and aged ones (> 1 month). The results were less reproducible on semi-porous surfaces and they became poor on porous surfaces, with no observable ridge details. Bergeron also proposed to replace methanol with water, but the results were not as good as with methanol. Finally, he observed that TiO_2 spraying can be used in sequence if it is applied after the classical blood reagents. No other forensic science publications refer to the application of TiO_2 to detect blood marks.

The underlying mechanisms explaining the affinity of TiO_2 for blood were not described by Bergeron. However, some explanations may be found in the literature: Thurn and coworkers reported that the surface characteristics of nanometer-sized TiO_2 allow efficient conjugation to nucleic acids [19]. Moreover, larger TiO_2 particles can interact with the cellular membranes composed of phospholipid bi-layers and adhere to them [267]. More specifically, authors reported some affinity between TiO_2 and blood [268] or between TiO_2 and proteins through electrostatic interactions [269]. Rothen-Rutishauser and coworkers also showed that ultrafine TiO_2 nanoparticles (diam. 32 nm) can penetrate the membrane of red blood cells, whereas aggregates larger than 200 nm were seen attached to the membrane but not within cells [200]. All of these observations may help in concluding that sub-micron TiO_2 particles may penetrate red blood cells and interact with haemoglobin, explaining their ability to detect blood marks.

Finally, Choi and coworkers, following their global strategy to develop enhanced functionalized nanopowders, combined oleylamine with a fluorescent dye (perylene dianhydride) to form an entity that was then adsorbed onto TiO_2 nanoparticles to form a new powder exhibiting strong fluorescence at 650-700 nm, when excited at at 505 nm [270]. Compared to conventional magnetic fluorescent powders, the nanopowder was slightly weaker in fluorescence intensity, but produced significantly less background development, resulting in good contrast between the fingermarks and the substrates.

In unpublished works, Saunders investigated the application to latent fingermark development of the TiO_2-based ITEK-RS process, which is a photographic process for obtaining silver images by silver ion physical development using TiO_2 as a light-sensitive component [271]. Using plastic weighing boats with latent marks placed on them as test samples and diluted white paint (brought to a pH of about 3 with citric acid) as the source of TiO_2, the following sequence gave excellent fingermark development: add TiO_2 (in suspension) to the sample, remove the liquid, expose the sample to UV radiation, add a weak version of Ag-PD. It works as follows, TiO_2 adheres to the secretion residue and is then UV-activated (daylight works). This activated TiO_2 reduces the silver ions in the Ag-PD and thus creates nucleating sites for silver physical development.

4.9. Zinc-based nanoparticles

Zinc oxide (ZnO) is generally used as a white pigment, but also for its photoluminescence properties, with emission peaks centered at 380 nm (UV) and 587 nm (visible). Similarly to titanium dioxide, ZnO has extensively been used in small particle reagent (SPR) formulations

to detect latent fingermarks on non-porous surfaces (wet powdering) due to its white color [265]. More recently, scientific works have considered the use of ZnO to detect fingermarks by taking advantage of its visible fluorescence. The first one consisted in the use of ZnO as a fluorescent pigment to be dry-dusted or applied as an SPR, on non-porous surfaces [45], The second one consisted in a modification of the classical multimetal deposition (MMD) procedure to produce *in situ* luminescent fingermarks on non-porous substrates [243] (see §4.4).

Since the use of ZnO nanoparticles in the context of the MMD method has been previously described, this section will focus on the dusting powder application reported by Choi and coworkers [45]. Starting from published procedures for obtaining nanostructured ZnO particles, the authors finally obtained particles in the size range of 1 to 3 microns. Even if the synthesized particles cannot be considered as nanoparticles, this application is worth being cited since a mechanical grinding took place before application, so that we can assume that nano-sized particles were finally obtained. ZnO particles were dusted and applied as small particle reagents. Detected fingermarks were characterized by a visible fluorescence when illuminated by long-range UV light source. ZnO-based SPR gave good results for all of the tested surfaces (glass, polyethylene, aluminium), while dry dusting led to some background staining on the polyethylene surface (Figure 28). When compared with conventional commercial powders, ZnO particles were less luminescent but showed excellent ridge detail, and with minimum background staining. The authors also tried to dope the powder using lithium ions, to enhance the visible luminescence, but this did not significantly improve the results.

5.0. Conclusions

The use of micron-sized particles for latent fingermark development has been around for over a century. Such particles include those in powder form and those suspended in solution. However, nano-sized particles, which are considerably smaller (their size ranging from a few nanometers to a few tens of nanometers) and whose small size provides them with some fascinating properties, are new to the fingerprint community. This chapter explored some of these properties, as well as some of the secretion residue properties, and showed how nanoparticles can be used to bind some components of secretion residue. This chapter may consequently provide the basis for developing new and original visualizing techniques.

About nanoparticles, we showed that some of the unique and important properties encompass their size, their optical properties, and their ability to have their surfaces modified. Photoluminescence can be an inner property, arising from the nature and composition of the nanoparticle, such as for quantum dots (a class of semi-conducting nanoparticles luminescent by themselves and whose emission wavelength depends on the particle size), or can be introduced after a dye-doping process, such as for silica nanoparticles. Physico-chemical properties generally arise once nanoparticles are put in aqueous solutions, with the presence of charges whose value varies according to the pH. However, the most significant property is certainly the ability of nanoparticle to get easily functionalized with molecules bearing specific functions. These molecules are generally chemically bonded to the particle surface and can be used to target numerous chemicals in latent residues during the detection process.

About the secretion residue, we learned in this chapter that the latent residue contains components that are not removed by water and that these water-insoluble components may become charged in solutions according to the pH. Thus, nanoparticles that are negatively-

charged at a low pH can potentially bind electrostatically to the positively-charged residue. Two well known techniques that rely on this property are the multimetal deposition (MMD) technique and silver physical development (Ag-PD) where colloidal gold and colloidal silver, respectively, are electrostatically attracted to the residue. We also learned that nanoparticles can be functionalized with lipophilic molecules so that, in a non-aqueous medium, they can get attracted to the lipid components of latent residue via hydrophobic interaction. Recent works involving gold nanoparticles functionalized with n-alkanethiols are an example of this.

About the development of new techniques, we showed that one should follow the usual three-step approach, which are: (1) determining which components of latent fingermark residue to target for visualization, (2) determining how to target these components, through the use of functionalized nanoparticles, and (3) making sure these substances do not create background interference. Finally, the choice for adequate optical properties (linked with the inner core composition or doping) is to be dissociated from the targeting mechanism (linked with the outer functionalization).

This chapter finally presented a thorough review of the several techniques based on nanoparticles and used for visualizing latent fingermarks. Numerous novel techniques were developed over the last 10 years, with a sharp increase in interest since 2004. We showed that a large variety of atomic compositions exists, including silver (Ag), aluminium (Al), gold (Au), europium (Eu), cadmium (Cd), iron (Fe), titanium (Ti), and zinc (Zn). The newly-developed techniques involve mainly nanoparticles dispersed in solution, but some report the dusting of dried nanoparticles. However, their use as powder carries a warning regarding the health hazards associated with their extremely small particle size. Nanoparticles were shown to be able to detect conventional latent fingermarks, as well as bloody ones or contaminated

ones (e.g., by drugs), on a wide range of substrates. The immunodetection of some secretion components (or contaminants) is also of rising interest by the use of antibody-functionalized nanoparticles.

Despite their demonstrated efficiency (in terms of selectivity or sensitivity) to detect fingermarks, only few of the presented techniques are actually used for casework application. It is only possible to cite those involving gold (i.e., MMD) and silver (i.e., Ag-PD). On the contrary, the great majority of the newly-developed techniques are still being investigated. Indeed, even if they are currently being successfully used for visualizing latent fingermarks on diverse surfaces under controlled conditions (using fresh or enriched marks sometimes), they still require making their proof on actual conditions by comparing with conventional reagents. For some of the published techniques, their intrinsic composition or application mode constitutes a major problem hampering their large-scale development (such as cadmium-containing quantum dots, or powdering of dried nanoparticles). This last step is required for the techniques based on nanoparticles to join the range of techniques commonly used by forensic scientists.

6.0. Acknowledgments

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Table captions

Table 1: Variation of particle parameters (mass, volume, edge length, areas and energies) with particle size.

Figure captions

Figure 1: Illustration of the evolution of the precursor concentration with time in the case of a homogeneous growth of nanoparticles. Nucleation begins only once a critical concentration value is reached. When the concentration of solute falls below this limit, only growth keeps proceeding. (Image source [86])

Figure 2: Formation mechanism of gold colloids in the citrate-reduction process, as proposed by Pong and coworkers [50]. Early in the process, gold aggregates (step a) self-assemble to form an extensive network of nanowires (steps b to d), explaining the dark-blue transient color. At a certain point, the network undergoes fragmentation into small segments to finally form individual, and spherical, gold nanoparticles (steps e to f). (Image source [50])

Figure 3: Illustration of the "electric double layer" of a colloidal particle (positively-charged) in aqueous suspension. The double layer is composed of the Stern (or Helmholtz) layer, which contains the strongly adsorbed counterions, and the Gouy layer, which is more diffuse than the first one in terms of ion and counterion concentrations. (Image source [33])

Figure 4: Schematic representation of a D.L.V.O. potential between two surfaces or particles [100,101]. According to this model, a "repulsion barrier" is created when combining the attractive van der Waals potential (V_A) and the repulsive electrostatic potential (V_R). This potential barrier has to be overcome before the aggregation of two colliding particles can occur. (Image source [33]).

Figure 5: The zeta potential progression of Schnetz's colloidal gold solution according to a decrease of the pH (blue curve), and stabilization role played by the addition of Tween 20 into the solution (orange curve). Caution: the X-axis is inverted, with the aqueous solution being more acidic as the axis progresses on the right. Colloidal gold has been synthesized according to Schnetz and Margot [25], and the pH is decreased by adding 0.1 M citric acid. At some point, the zeta potential falls inside the ±30 mV instability zone. Without Tween 20, the sol turnes purple, due to the aggregation of gold nanoparticles, at a pH of 1.70 (unpublished results). With Tween 20, the sol remains stable even if its zeta values are located within the electrostatic instability zone across the whole pH range.

Figure 6: (a) Evolution of the luminescence emission for cadmium telluride quantum dots of increasing size (from left to right), illuminated under UV radiation (300–400 nm) using a Mini-Crimescope 400. (b) Emission spectra obtained for the samples shown using a Perkin Elmer LS-50B luminescence spectrophotometer. The spectra were normalized to 1.0 to illustrate the progression of the maxima of intensity to higher wavelengths as the quantum dots are growing in size. The samples were obtained by removing a small amount (2.5 mL) of concentrated quantum dots from the reaction mixture at different reaction times. (Image source [41])

Figure 7: Illustration of the different emission wavelength ranges according to the atomic composition of the most commonly encountered quantum dots. On the top are also represented the areas of biological interest, mainly located in the visible – near infrared regions of the spectrum. (Image source [20])

Figure 8: Illustration of the functionalization strategy, which involves functionalizing the outer surface of nanoparticles with ligands to increase their physico-chemical properties (affinity) and chemical behavior towards secretion residue.

Figure 9: Illustration of how metal nanoparticles (up) and silica nanoparticles (down) can be functionalized using well-adapted ligands, namely, alkanethiol for gold and 3-amino-propyltriethoxylsilane for silica.

Figure 10: Illustration of the evolution of the charge on the residue according to the pH. Red, blue and grey zones correspond to positive, negative and neutral states, respectively. The "green-grey" zone corresponds to the pH region where the residue has the least charge, since there is a competition between the positively- and the negatively-charged components.

Figure 11: Evolution of the electrostatic force between gold colloids and proteins contained in the residue (in the context of multimetal deposition). The force is attractive (negative value) below the isoelectric point of proteins (pI), since gold nanoparticles are negatively-charged (Q_{gold}) and proteins start to be positively-charged (Q_{prot}). Conversely, the force is repulsive (positive value) above the pI, since gold colloids and proteins are negatively-charged. In the equation, K is a constant whose value depends only on the permittivity of the medium into which the nanoparticles are dispersed.

Figure 12: Evolution of the size and charge of silver colloids in the context of the physical developer. The colloids are first negatively-charged (due to the adsorption of citrate ions), but as they grow in size, cationic surfactant molecules begin to surround the colloids so that the charge is reversed towards positive values.

Figure 13: Scanning electron microscope image of a silver colloid particle on a paper fiber bearing fingermark residue.

Figure 14: Illustration of n-octadecanethiol and the corresponding functionalized gold nanoparticle (left), and of n-octadecylamine and the corresponding functionalized CdSe/ZnS quantum dot (right), as used by Sametband and coworkers to promote lipophilic interactions with the lipid fraction of latent fingermarks [30].

Figure 15: Formation of a peptide bond between a carboxylic acid and a primary amine. The reaction usually needs to be catalyzed through the activation of one of the two groups to occur quickly.

Figure 16: Schematic representation of the dioctyl sulfosuccinate-capped CdS quantum dot that has been used by Menzel and coworkers [221] to detect fingermarks on non-porous surfaces. The illustrated fingermark (from [221]) has been developed by cyanoacrylate/CdS nanocrystal staining on a soft drink can.

Figure 17: Schematic representation of the thioglycolic acid-capped CdSe quantum dot that has been used by Wang and coworkers [43] to detect fingermarks on the sticky-side of adhesives tapes. The illustrated fingermark (from [43]) has been developed on the adhesive-side of a black tape, at pH 8 for the left half and pH 11 for the right half.

Figure 18: Schematic representation of the thioglycolic acid-capped CdTe/Cds quantum dot that has been used by Becue and coworkers [41] to detect blood fingermarks on non-porous

surfaces. The illustrated fingermark has been developed by CdTe/CdS nanocrystals (left half) and by Acid Yellow 7 (right half), which is a classical blood reagent; after [41].

Figure 19: Schematic representation of the amino-functionalized Eu_2O_3 nanoparticle that has been used by Menzel and coworkers [238] to detect fingermarks on non-porous surfaces. The europium-based core has been surrounded by a silica shell to permit the functionalization of the outer surface with amino groups.

Figure 20: Schematic representation of the ‘‘two-step’’ process characteristic of the multimetal deposition (MMD) process for detection latent fingermarks. In the case of the classical MMD method, metallic silver is used to coat the gold nanoparticles (NPs). For the single-metal deposition (SMD) method, gold NPs are grown by selective gold deposition. Finally, for the luminescent version of the MMD method, ZnO is deposited *in situ* on the gold NPs to obtain a luminescent structure. (Image source [243])

Figure 21: Schematic representation of the ZnO-capped gold nanoparticles that have been used by Becue and coworkers [243] to detect fingermarks on non-porous surfaces. (a) Fingermarks deposited on a black polyethylene bag (left mark) and on black polystyrene packaging (right mark), detected according to the MMD_{lumin} protocol [243]. A 300–400 nm excitation light source has been used. (b) Fingermark deposited on commercial packaging and detected according to the MMD_{lumin} protocol. In visible luminescence mode (left), the substrate presents a strong luminescence, thus reducing the contrast with the mark. When observed in the UV-range, the same mark is visible with good contrast due to the luminescence of ZnO in this range of the electromagnetic spectrum. The substrate presents no luminescence in this range of wavelengths (unpublished results).

Figure 22: Schematic representation of the alkanethiol-capped gold nanoparticles (Au-NP-C_{18}) that have been used by Sametband and coworkers [30] to detect sebaceous fingermarks on porous and non-porous surfaces. The illustrated fingermark (from [30]) has been deposited on paper and developed with silver physical developer, Ag-PD, only (left half) and by Au-NP-C_{18} followed by Ag-PD (right half).

Figure 23: Schematic representation of "protein A / antibody"-functionalized gold nanoparticles that have been used by Leggett and coworkers [156] to detect fingermarks from smokers on glass. The illustrated fingermark (from [156]) has been obtained from a male smoker after sweating for 40 min and detected using the antibody-functionalized nanoparticle and Alexa Fluor 546 as luminescent marker.

Figure 24: Schematic representation of the oleylamine-functionalized gold nanoparticles that have been used by Choi and coworkers [211] as a nanopowder to be dusted on fingermarks. The illustrated fingermarks (from [211]) are fresh ones that have been deposited on glass and dusted using a conventional black powder (left half) or using the gold nanopowder (right half).

Figure 25: Schematic representation of the dye-dope silica nanoparticles that have been used by Theaker and coworkers [44] as a nanopowder to be dusted on fingermarks, or as a suspension in water. The illustrated fingermarks (from [44]) are on glass that have been detected using Rhodamine 6G-doped silica nanoparticles in an aqueous suspension (left mark) or as a dusting powder (right mark).

Figure 26: Schematic illustration of the application protocol for the UK silver physical developer (Ag PD). The procedure begins with an acid pre-wash to remove the calcium carbonate contained in some substrates and is followed by the actual physical development step, which involves depositing silver colloids and amplifying them by reducing silver on their surface.

Figure 27: Fingermark on a counterfeit U.S. banknote developed using a silver physical developer (and enhanced with a weak NaOCl bath) with interfering background (left) and enhanced by the KI method (right). (Image source [259])

Figure 28: Three-week-old fingermarks on polyethylene, developed using zinc oxide as a nanopowder (left) and as a small particle reagent (right). The samples were illuminated at 350 nm and observed using a 570 nm long-pass filter. (Image source [45]).

7.0. References

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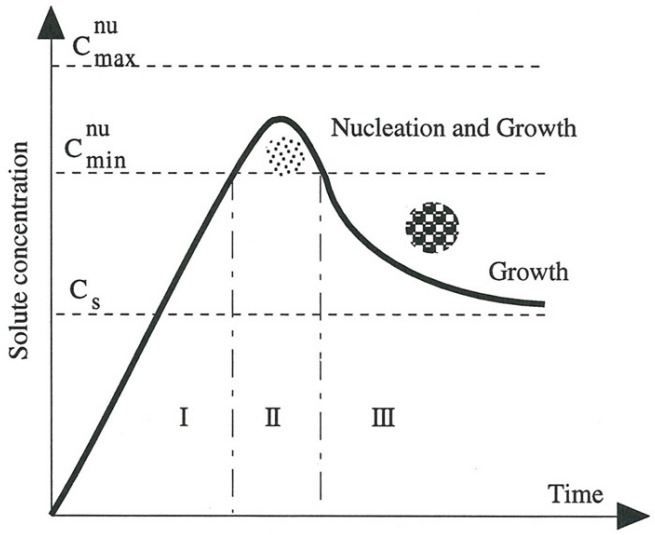
Figure 1



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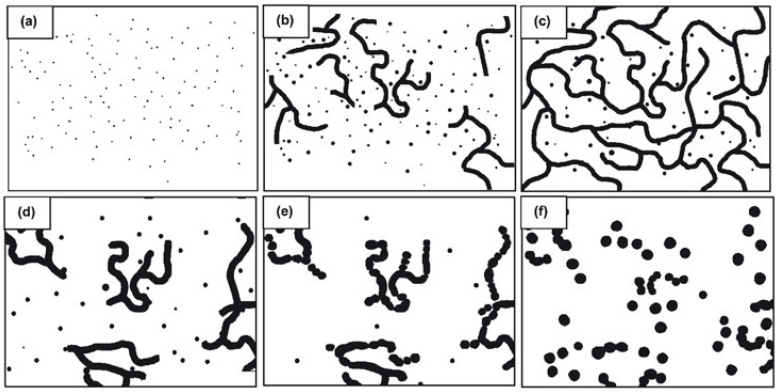

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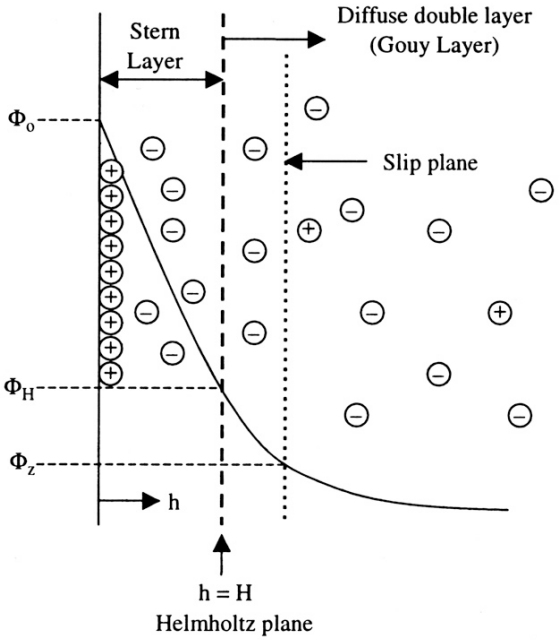

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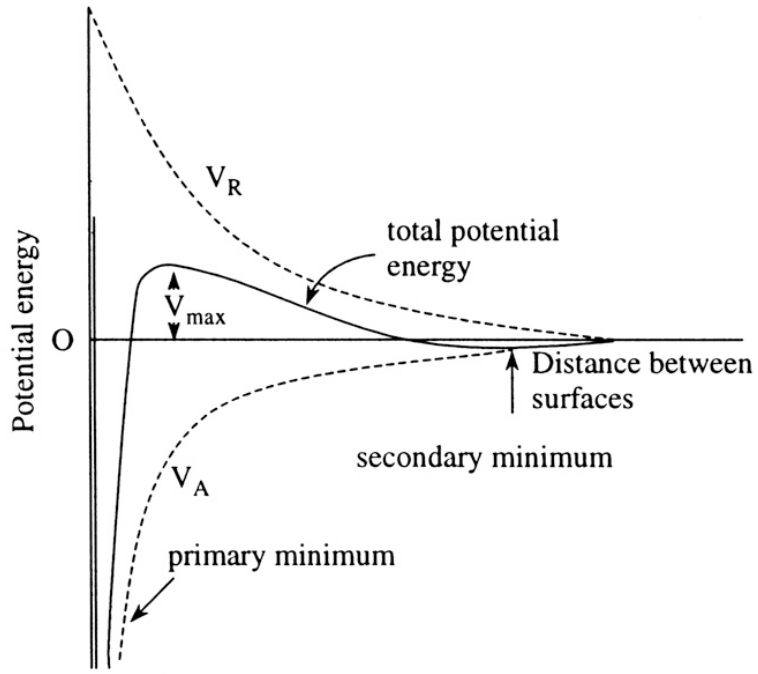

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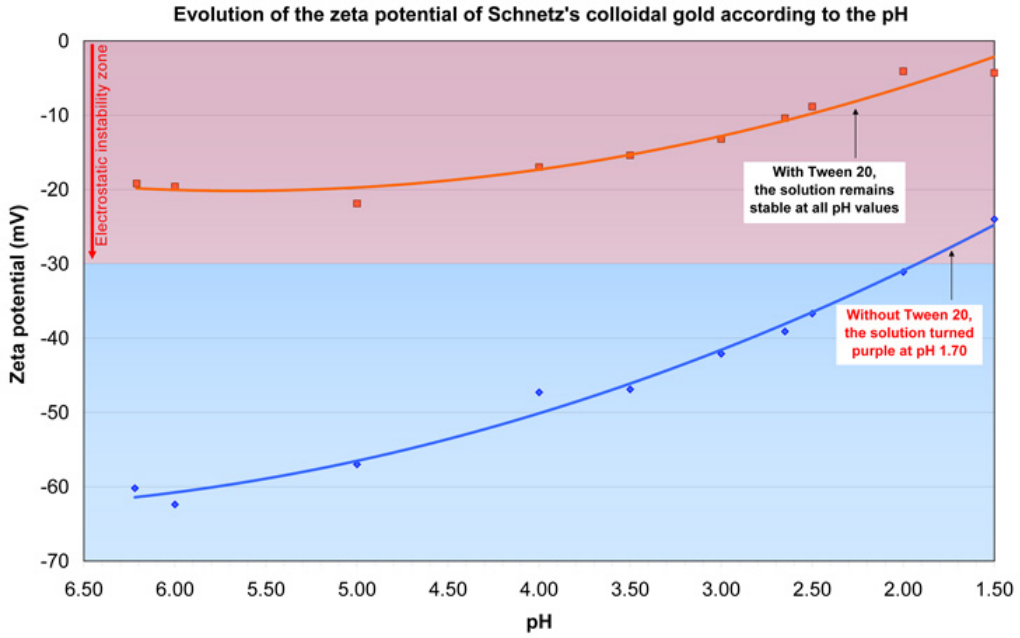

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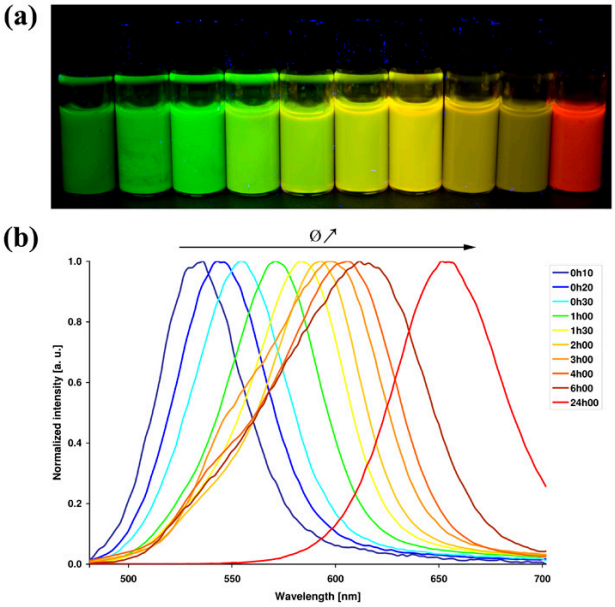

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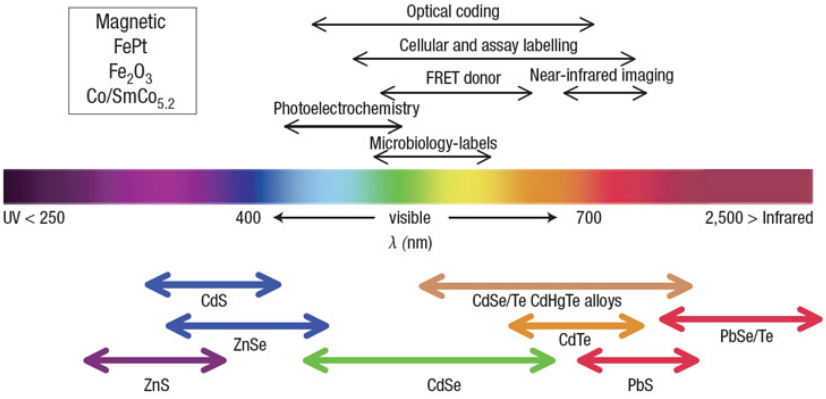

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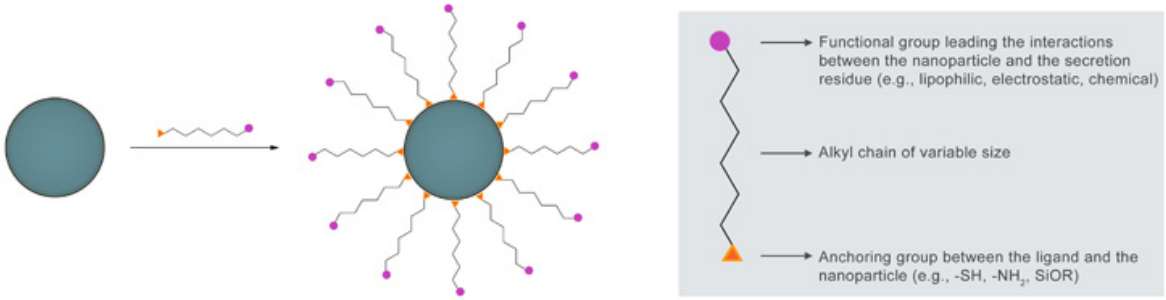

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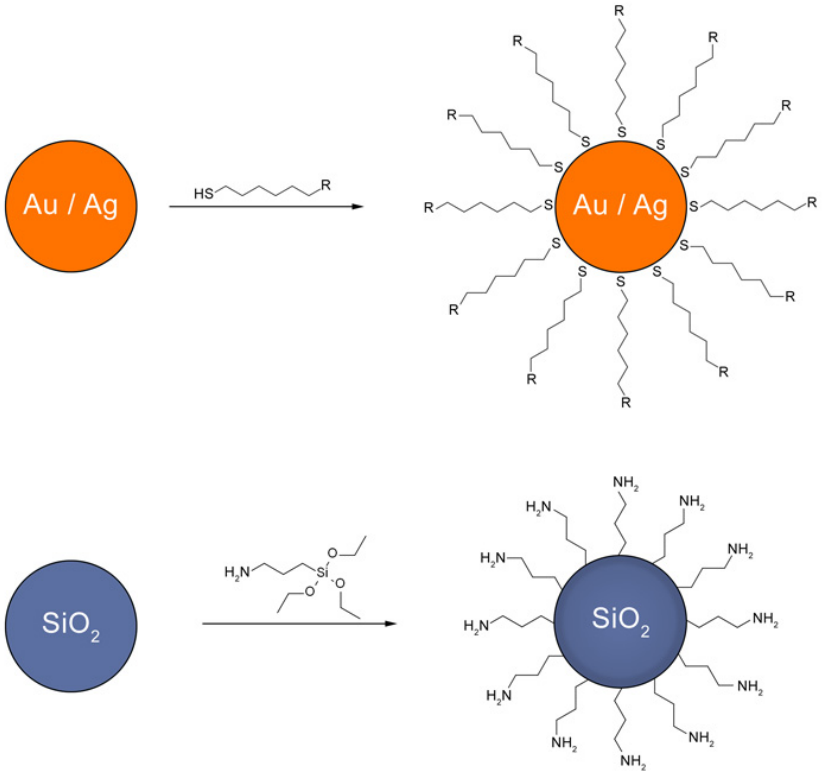

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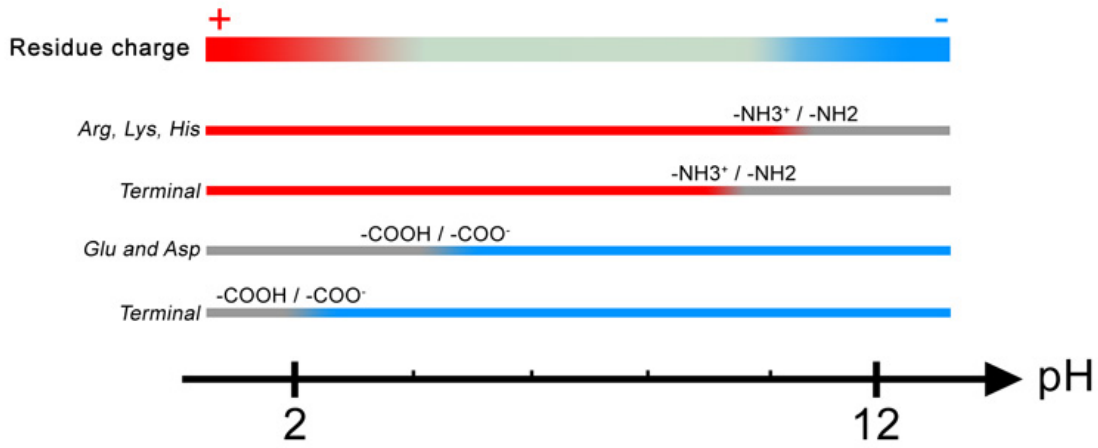

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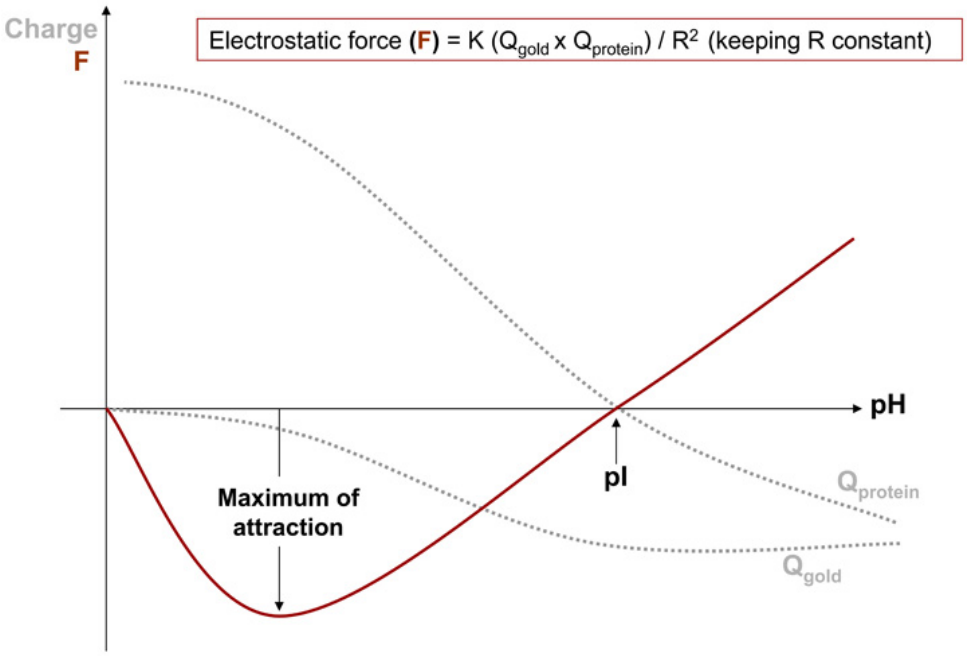

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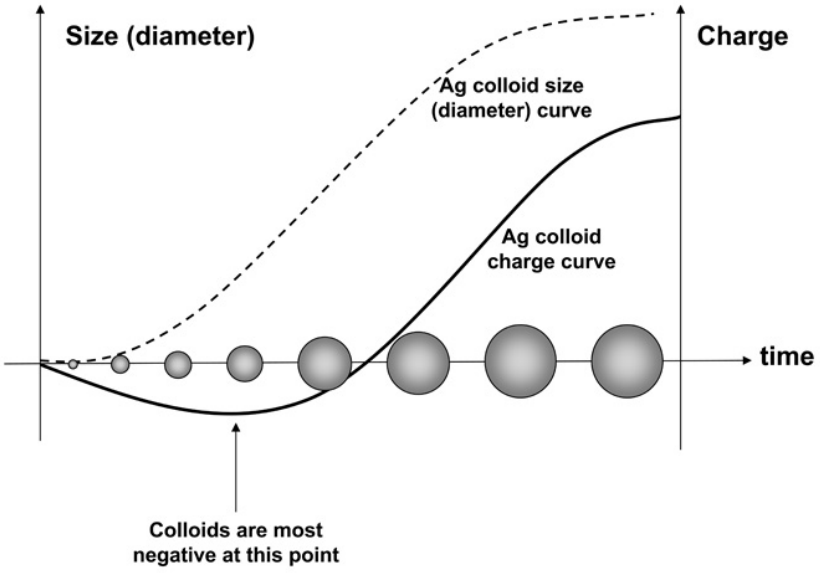

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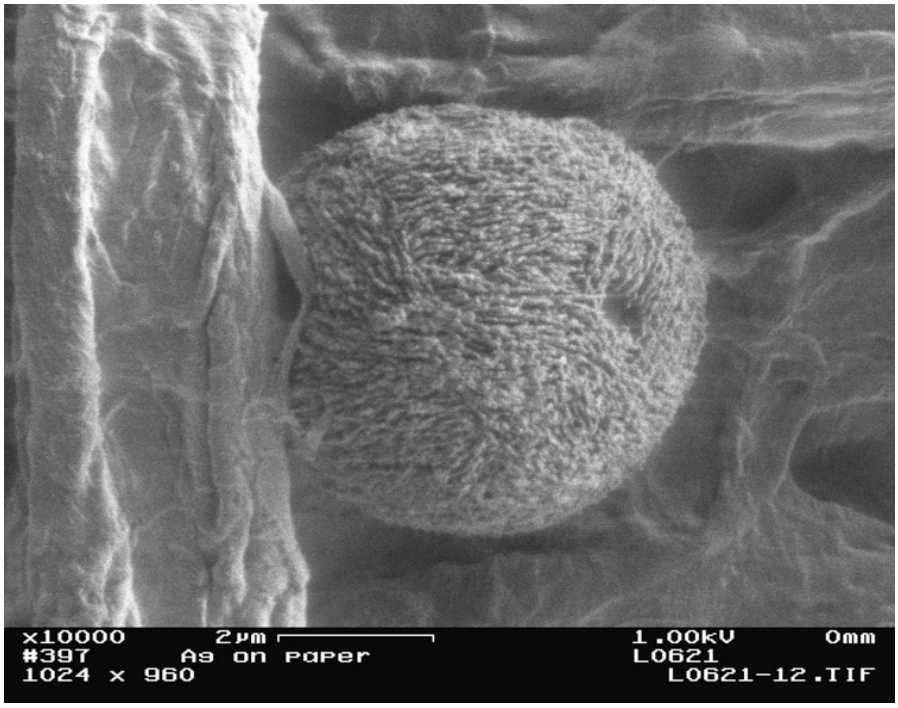

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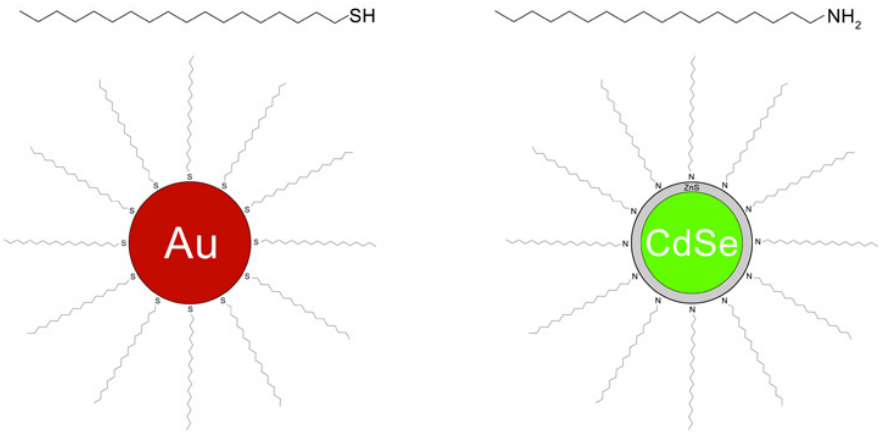

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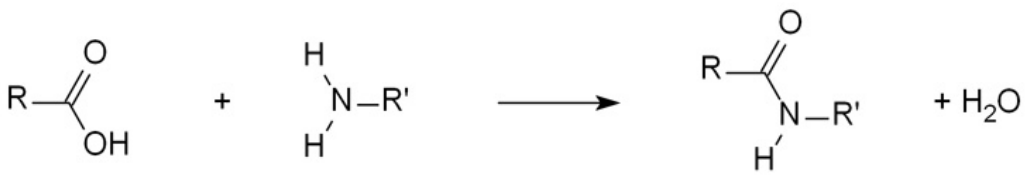

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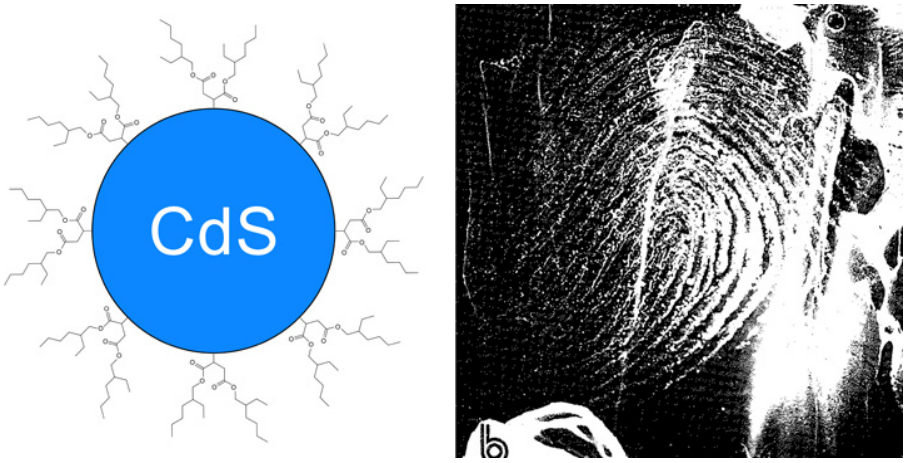

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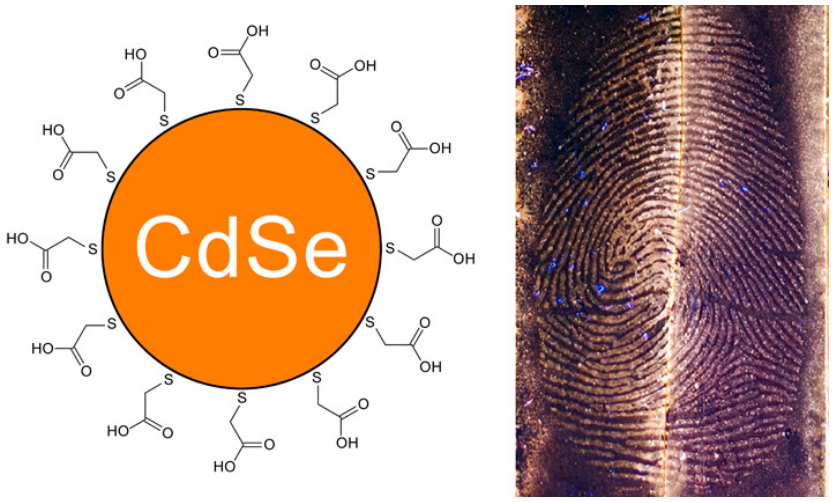

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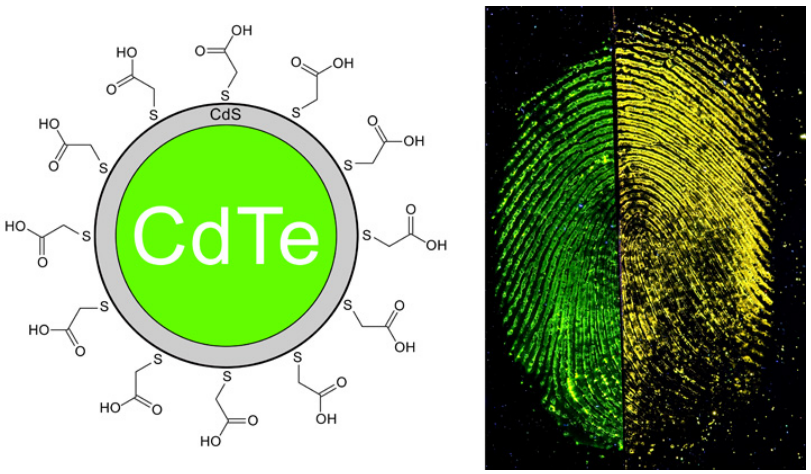

Figure 19

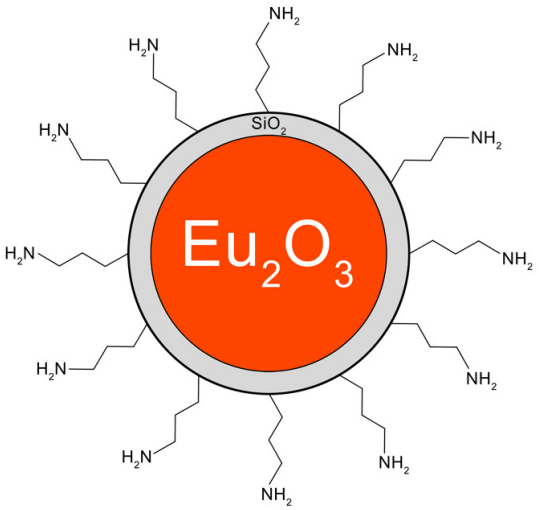

Figure 20

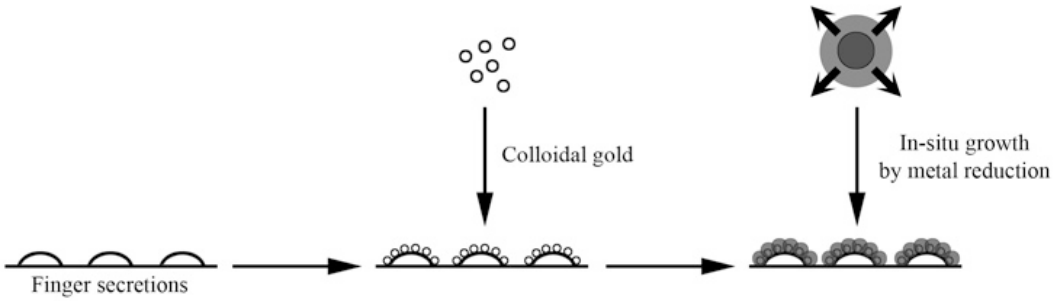

Figure 21

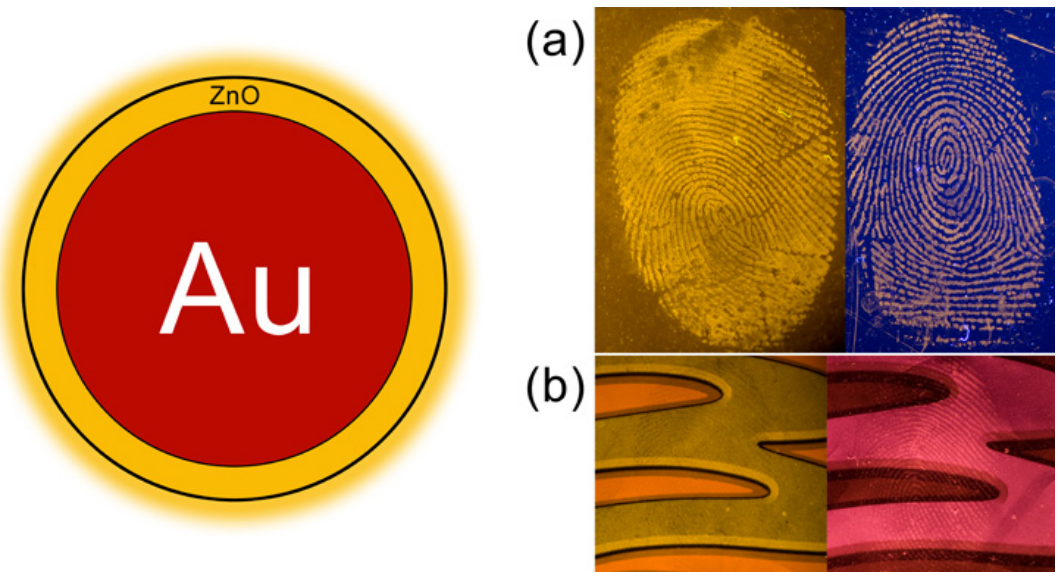

Figure 22

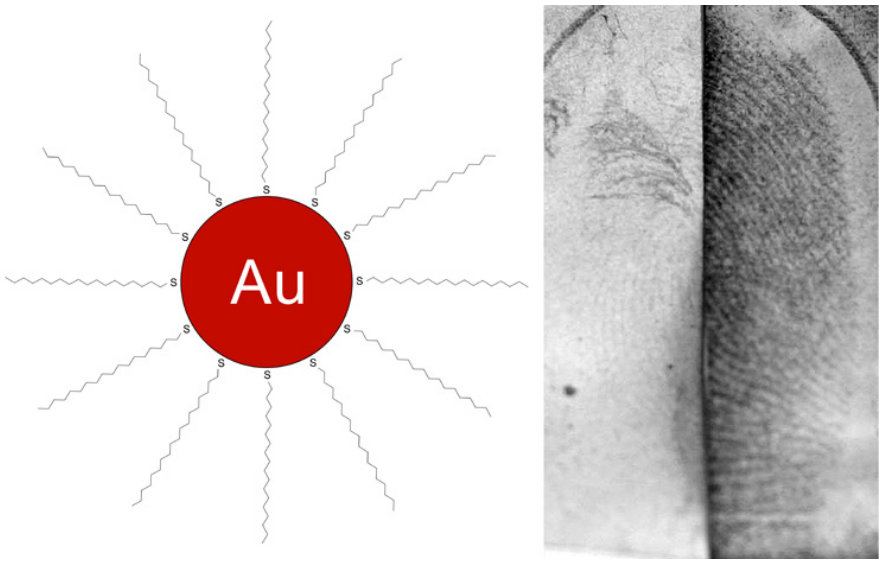

Figure 23

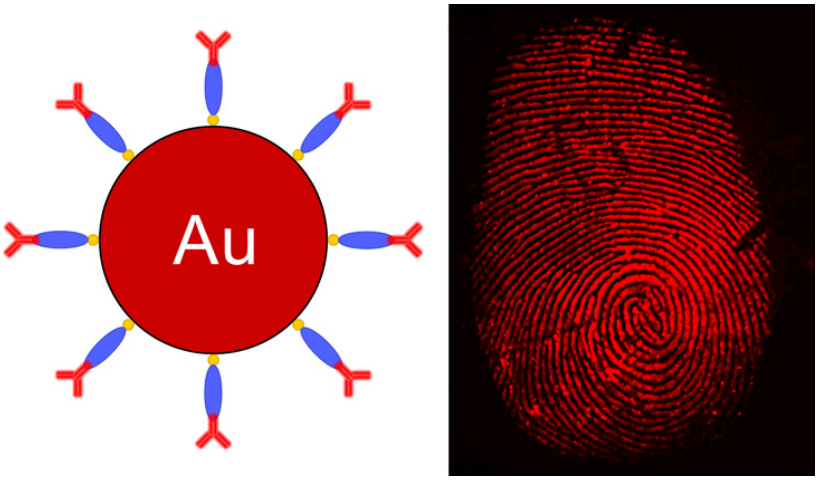

Figure 24

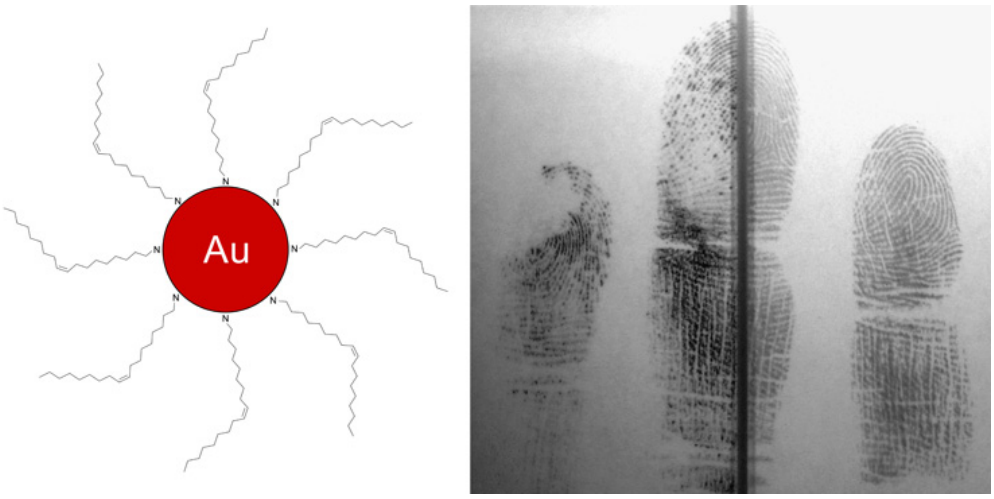

Figure 25

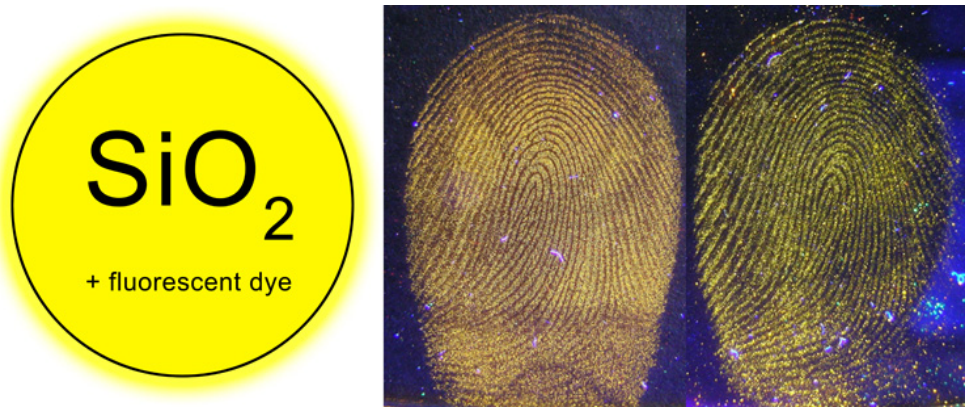

Figure 26

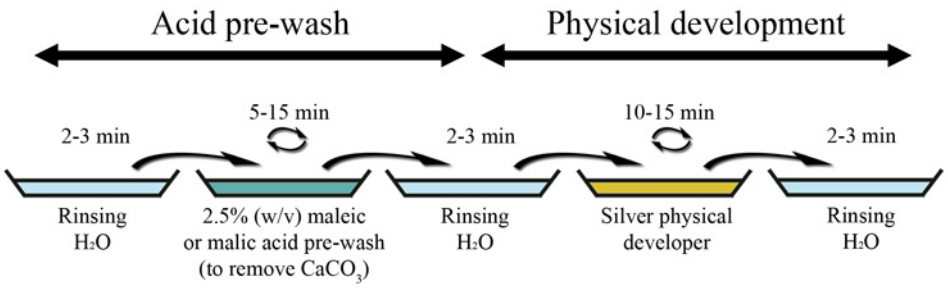

Figure 27

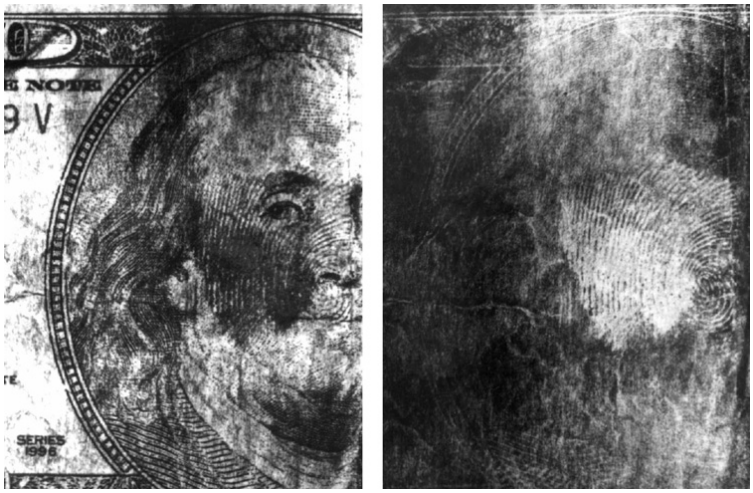

Figure 28