

REVIEW ARTICLE

Role of Fluorescent Substances in Development of Latent Fingerprints: A Review

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ABSTRACT

Fingerprints are one of the crucial pieces of evidence in criminal investigations. As fingerprints are majorly found in latent form on the surface, it is necessary to develop those latent fingerprints appropriately without destroying them or leaving out any detail. There are plenty of methods for identifying hidden finger impressions. The powder dusting method, ninhydrin, iodine fuming, cyanoacrylate etc., are traditional methods. Though these procedures help to develop the latent fingerprints, they have some drawbacks such as sensitivity, low contrast, and selectivity as well as high toxicity. To overcome this inadequacy, advanced techniques have been developed using different chemicals and nanoparticles such as metal nanoparticles, fluorescent nanoparticles embedded with quantum dots, rare-earth upconversion nanoparticles etc. The fluorescent nanomaterials enhanced all three levels of fingerprints and provided the minute details of latent fingerprints. This review paper focuses on the role of fluorescence-based methods used for the enhancement of the latent fingerprint and their advantages over traditional methods. As compared to other approaches, fluorescent nanomaterials can obtain optimal contrast quality, enhancement, better sensitivity, and selectivity while exhibiting lower toxicity, less autofluorescence interference, and low background inference.

KEYWORDS | lie detector, forensic evidence, polygraph, narco test

INTRODUCTION

Fingerprint impression is the most crucial evidence in criminal investigation. Fingerprints can be left at the crime scene when a person touches an object or surface. It helps in identifying an individual whether the suspect was present at the crime scene.¹ Sweat from the pores on the friction ridge skin of the hands leave finger impressions on objects and surfaces. Pores abound in the ridges of the fingers. Sweat from these pores is deposited in the form of outlines when the fingers touch any surface or object. It acts as a replica of the ridge patterns of the fingers.² Sweat is colorless; so when it is deposited on a surface it leaves behind colorless impressions known as latent fingerprints.

Secretions from the eccrine (sweat), sebaceous, and apocrine glands on the hand, head, and nose make up latent fingerprint residues. Sweat consists of 0.5 percent minerals, approximately 0.5 % organic compounds, and 98 percent water. Sugars, urea, creatinine, Proteins, uric acid, amino acids, lactic acid, and choline make up eccrine sweat, while wax esters, glycerides, sterol esters, fatty acids, and squalene make up sebaceous sweat.³

Latent fingerprint impressions which are present at the crime scene, need to be developed using an appropriate technique. The powder method has been used most widely to develop fingerprint impressions at the crime scene. The powder method includes metallic and

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magnetic powders as well. These methods also possess certain disadvantages like high toxicity, background interference, contrast, selectivity, and less sensitivity with fewer development of all the ridges of finger impressio.⁴ Apart from the traditional powder methods, there are chemical techniques that have been used like ninhydrin, iodine fuming but just like powder methods these techniques also have drawbacks.⁵

To overcome this inadequacy, researchers have been exploring many new techniques to enhance the quality of hidden finger impressions and make it cost effective, and providing better efficacy to assist in the investigation by identifying the suspect. The advanced techniques have been developed using different chemicals and nanoparticles such as metal nanoparticles, fluorescent nanoparticles embedded with quantum dots, rare earth upconversion, etc.⁶

Fluorescent Nanomaterials

The fluorescent nanomaterials enhanced all three levels of fingerprints and heightened the minute details of hidden finger impressions. As compared with other approaches, fluorescent nanomaterials can obtain optimal contrast quality, enhancement, better sensitivity, and selectivity while exhibiting lower toxicity, less autofluorescence interference, and low background inference. Oily substances are found in dormant finger impressions due to the normal human habits of touching the hair and face. As a result, if a fluorescent reagent would diffuse into the oily substances without rubbing out the hidden finger impressions with the substrates, it could be counted as an adaptable probe for latent finger impressions fluorescence imaging.⁷ Strong fluorescence can be generated by fluorescent materials that have engrossed precise electromagnetic radiation such as ultraviolet, near-infrared, or visible light.⁸ When working with multi-coloured or reflective surfaces, where contrast can be an issue with conventional fingerprint powders, the use of fluorescent methods to produce hidden finger impressions has an inexpensive benefit.⁹

Characteristics of Fluorescent Nanomaterials

Due to their peculiar ocular characteristics, the use of fluorescent nanomaterials like up conversion nanomaterials and quantum dots for the enhancement of latent finger impressions

has gotten a lot of attention.¹⁰ When fluorescent nanomaterials are utilized for hidden finger-marks growth, they have many benefits, including low toxicity, high developing contrast and selectivity, and high sensitivity.^{11,12}

Toxicity

Some components in quantum dots, like Cadmium, have the potential to be toxic. Furthermore, certain quantum dots have the potential to originate irritation and aversion.¹³ Modification in the surface by adding a layer of silica dioxide was documented to reduce the toxicity of quantum dots to a large extent.¹⁴ The upconversion nanomaterials modified at surface level contain low toxicity.¹⁵ The near infrared light-based excitation of upconversion nanomaterials is less harmful to the DNA present in the remaining finger marks, hence, DNA analysis can be performed for the identification of an individual. The use of upconversion and quantum dots are suitable options as they opt for less toxicity or sometimes no toxicity.⁹

Contrast

The up-conversion nanomaterials and quantum dots can release visible fluorescence with high intensity under near-infrared and ultra-visible light. Strong fluorescent emissions can boost the emerging signal while reducing the distraction of the background color, resulting in high enhancing contrast.^{11,16} Furthermore, since near-infrared lights emit low energy radiation, they do not cause background fluorescence to be emitted from substrates, eliminating the possibility of background color distraction and, as a result, allowing for high evolving contrast.⁹ Because of their strong fluorescent properties, they can achieve a high emergent contrast by increasing the evolved signal and decreased background colour distraction when used for latent fingerprint growth.

Selectivity

Surface alteration is a versatile and efficient method for achieving high selectivity of finger impression. Surface modification can change the electric charge of the fluorescent nanomaterials, allowing them to bind to precise remains in finger impressions through electrostatic adsorption for high emerging selectivity.¹⁷ Furthermore, these fluorescent nanomaterial surfaces can be

modified using the number of functional groups such as amino, carboxyl, and aldehyde. Chemical reactions allow them to selectively mark a particular component in finger marks, resulting in high selectivity.¹⁸ By further addition of molecules like lysozyme, the binding aptamer can help in the conjugation with residues of finger impressions containing lysozymes leads to high selectivity.¹⁹

Sensitivity

Upconversion and quantum dots are usually small in size. In the case of upconversion fluorescent nanomaterial, the diameter is not more than 100 nm, and in the case of quantum dots, the diameter is not more than 10 nm. The ridge information, such as the fingerprint patterns, or individual characteristics like- termination points, bifurcation, dots, ridge ending, and the location of sweat pores, will not be heavily shielded when using these small-sized fluorescent nanomaterials for the enhancement of the hidden finger marks and gives high sensitivity.¹¹ Furthermore, these nanomaterials have a spherical shape that can be adjusted through the synthesis process. Surface modification may also be used to adjust the tackiness of the material. As a result, the adsorption on the finger mark remains can be modified, and the emerging sensitivity can be improved even more.^{20,21}

METHOD & MATERIALS

Diatomaceous earth is made up of diatoms' remains and is found in the form of powdery silica. Diatoms vary in size from approximately 5 microns to 1000 microns. There are more than 200 genera of living diatoms which are estimated, and almost 100,000 species exist.²² Diatomaceous earth's fine-grained, highly porous, and lightweight nature makes it suitable for use as an absorbent, insulation medium, mild abrasive, and agent in DNA purification and extraction.²³ Electrostatic force and hydrogen bonds can firmly attach the fluorophores of some cationic dyes present in this material.²⁵ Diatomaceous earth would be an excellent modulator for the generation of solid and photostable fluorescence because of the shielding effect of silica walls. Therefore, the selection of appropriate fluorescent dyes containing cationic fluorophores is critical. As a standard xanthene dye, rhodamine B is commonly used in solid-

state lasers, optical filters, and other applications.²⁶ Even when encapsulated in a matrix material, it is well recognized for excellent spectroscopic features such as good fluorescence quantum yield and high photostability.²⁷ Rhodamine B's longer excitation wavelength allows it to be used as an excitation light source in the green region rather than the UV or violet-blue region, which is safer for humans and allows for better conservation of trace evidence such as DNA in fingerprint deposits. For the preparation of novel fluorescent fingerprint powders, diatomaceous earth and Rhodamine B may be excellent silica hosts and fluorescent hosts.

A series of Rhodamine B-diatomaceous earth composites have been successfully prepared as novel fluorescent fingerprint powders using a green, simple, and versatile preparation method based on physical adsorption between cationic fluorophores and porous silica. The fluorescence characteristics of the composite powders change with the amount of Rhodamine B present, due to the different accumulation phases of functional groups in the composite powders. The current research was the first to demonstrate a new mechanism for developing and improving latent fingerprints by using fluorescence properties of as-prepared fingerprint powders by qualitative and quantitative analyses. According to the mechanism, a photo recording and enhancement system with optical devices (532 nm alternate light source, cell phone camera, and 580 nm long-pass filter) and image analysis techniques (channel separation with PhotoShop and grey analysis with Image) were developed.²⁸

Earth Upconversion Fluorescent Nanomaterials

Rare earth upconversion fluorescent nanomaterials (UCNMs) are materials that have been doped with rare earth elements. They emit a shorter wavelength light when excited by a longer wavelength light. When excited by NIR light, they produce visible light. UCNMs have a number of distinct attributes, including small emission spectra, low toxicity, and high intensity. They can also be chemically functionalized. Background fluorescent interferences are excluded since they can be excited using NIR light, resulting in increased evolving contrast. As a result, UCNMs show improvement for developing

latent fingerprints with high contrast, selectivity, and sensitivity. NaYF₄ co-doped with Yb³⁺-Er³⁺ ions (NaYF₄:Yb,Er) is the most widely used UC material today which is also capable of emitting the brightest UC fluorescence.²¹

Wang et al., also prepared the upconversion nanomaterials using NaYb_{0.98}F₄:Tm with the help of solvothermal technique. Generally, NaYF₄:Yb, Er UCNM production was focused on a single near-infrared to visible method that allows finger impressions to be observed by sensing visible light under near infrared light excitation. Otherwise, it can be prepared by dual method that is near-infrared to near infrared and near-infrared to visible technique. The synthesized upconversion nanomaterials had a versatile fluorescent marker quality and used a dual-mode production on porous, non-porous semiporous surfaces. This method produced the enhanced fingerprints with better contrast, high selectivity, and sensitivity under both near-infrared to near infrared and near-infrared to visible methods.²⁹

Bilayer systems based on conjugated polymers

Bersellini et al., suggested a new notion based on the electropolymerization of polypyrrole on surfaces such as gold, platinum, silver, and aluminum alloy (Ergal).³⁰ Hillman et al., used this technique to improve latent fingerprints on metallic surfaces like brass or stainless steel by electrodepositing conjugated polymers including Polypyrrole, Poly (3,4-ethylenedioxythiophene), and Polyaniline. The process in which the electrochromic material allows for the manipulation of optical properties (polymer color) by applying an electrical potential, has the efficacy to enhance the latent fingerprints. In spite of that, the visualisation of the fingerprint image under UV light is sometimes needed, particularly in case of dark or multicoloured backgrounds. Therefore, second layer of fluorescent conjugated polymer can be added to enhance the contrast.^{31,32}

Conjugated polymer shows advantages over molecular fluorophores, including high emission, low-cost synthesis, and low toxicity. A series of fluorescent materials based on conjugated polymers for a variety of applications has been synthesised by C.V. Costa et al., The precursor monomers of those conjugated polymers were insoluble in water.³³

The usage of an aqueous medium for electrodeposition of the polymer was one of the foundation approaches proposed by Hillman et al. This approach was based upon the assumption that the presence of fatty acids in the remains of the latent fingerprints serve as an insulating cover on which the polymer must not be deposited, resulting in a detailed finger impression imaging.³⁴

C.V. Costa, et al., strategized a technique for the latent fingerprint development based upon the conjugated polymers bilayer, containing first layer of polypyrrole as electrodeposition on a stainless steel having a latent fingerprint. The second layer made up of fluorescent poly (2'2'-2"5'-terthiophene which was electrodeposited on the first layer. This technique showed the detailed structure of latent fingerprints containing ridge pattern, class and individual characteristics. The fluorescent bilayer system interacts with the unexposed area of the substrate which helped in the enhancement of the contrast between surface and fingerprint, has low toxicity as materials used for the synthesis are less toxic in nature, and easy development of the polymer film using Galvanostatically and Potentiostatically methods. This technique combines UV and visible light for better enhancement of fingerprints and can be used as suitable one on stainless steel surface.³³

Quantum Dots

Cai et al., used an extremely fluorescent water-soluble cadmium-telluride quantum dots capped by mercaptosuccinic acid basic solution in 1–3 seconds to enhance hidden fingerprints on numerous nonporous exteriors. Mercaptosuccinic acid cadmium-telluride quantum dots showed the higher sensitivity and image excellence when developing dormant fingerprints.³⁵

Chen et al., worked on dual visual senser based on polymer dots that helped in imaging of fingerprints. They embedded ninhydrin into the Polymer dot matrix after scheming and synthesising two forms of near-infrared fluorescent polymers. The characterization of nanoparticles has been done by transmission electron microscope and dynamic light scattering. The fluorescence remained measured using fluorometer under 450 nm excitation and absorption spectra under UV-Visible spectrophotometer. The colorimetric and fluorescent dual-readout capabilities of

the Polymer dot assay to spot dormant finger impressions on absorbent and non-absorbent exteriors were demonstrated. The chemical groups were also imbedded onto the surface of the nanoparticle to examine the process responsible in the growth of fingerprint. The assay has been used to image hidden fingerprints on checks and note paper. This technique helped in detecting hidden fingerprints on all smooth surfaces with low background interference, high resolution, and contrast. It showed all the particulars of fingerprints from level one to three.³⁶

Conjugated polyelectrolyte dots have become a choice in bioimaging probes as they contain low cytotoxicity, strongly biocompatible, and have outstanding fluorescence brightness. Conjugated polyelectrolyte dots are made by dissolving water soluble conjugated polyelectrolytes in water to produce an aqueous colloidal solution. They are commonly found as particles like nano sized in water, despite their polar side chains increasing

their water solubility. This is because the polymer chains appear to accumulate in aqueous environments due to the inherent hydrophobicity and structural rigidity of the main chains. The Conjugated polyelectrolyte dots amphiphilic features can be precisely balanced with the help of surfactants with sufficient hydrophile-lipophile-balance values and then the fluorescent nanoparticles can be efficiently transferred to the oily phase of a latent fingerprint while the latent fingerprint remains intact. Kim et al. worked on different variety of Conjugated polyelectrolyte dots to develop the hidden fingerprints using fluorescent imaging probes. The hidden finger impressions could not be stained by the aqueous Conjugated polyelectrolyte dots colloidal solutions alone. The Conjugated polyelectrolyte dots nanoparticles were transferred directly to the hidden finger impressions when an acceptable surfactant was applied to the aqueous mixture and then sprayed onto the hidden finger impressions. These showed the extremely distinct fluorescent images of latent finger impressions. Cationic surfactant also helped in enhanced the dormant finger impressions and made them brighter. This technique is convenient, simple, and universal which helps in the higher visualization of hidden finger impressions.⁷

Non-metals Nanoparticles with Fluorescence Characteristics

Rajan *et al.*, synthesized the silica nanoparticles using rice husk by thermochemical treatment which were then dyed with natural dyes. Fourier-transform infrared spectroscopy, Field emission scanning electron microscopy, X-ray diffraction analysis, and forensic alternate light source were used to record and characterise the powders' photoluminescence. By producing dormant fingerprints left on various multicoloured substrates, the efficacy of three fluorescent variants of silica nanoparticles powders and industrial fluorescent powder was studied. Rice husk was successfully used to make spherical fluorescent silica nanoparticles. Amorphous spherical silica nanoparticles with an average crystallite size of approximately 200 nm were discovered during characterization studies of coloured silica nanoparticles. Once heat was applied and aged at room temperature, silica

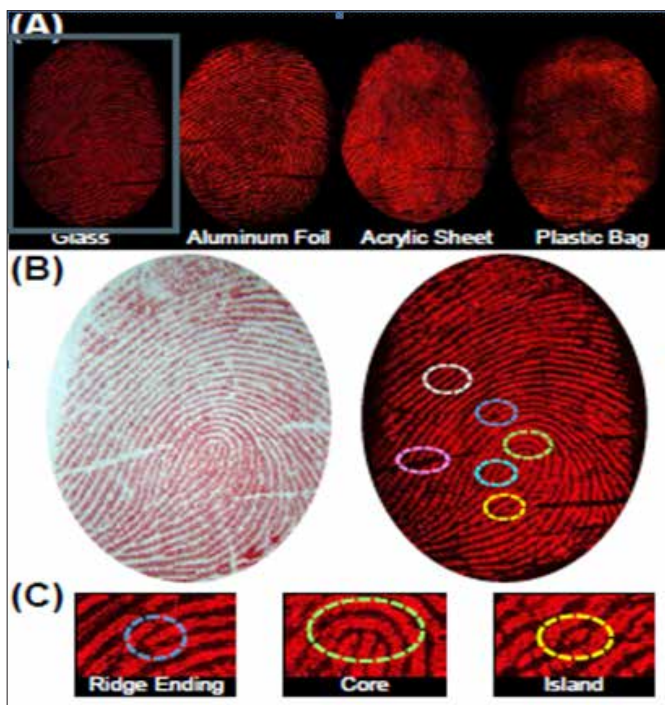


Figure 1: A) Hidden finger impression pictures enhanced using polymer dots on crystal, aluminum paper, acrylic piece, and plastic container. (B) finger impression assessment marked using a Polymer dots (right) and red inkpad (left). (C) Level one-three data, including centre, ridge ending, bifurcation, island, scar, and pore, are visible in high-resolution fluorescence images of latent fingerprints. A 450-nm LED light with an orangish filter was used to excite all fluorescence images. Copyright © 2016, American Chemical Society

nanoparticles doped with curcumin pigment showed the best stability and greatest fluorescence. Electron microscopy and surface tests results on different surfaces showed that the dye doping method did not compromise the efficiency of the coloured silica nanoparticle. The results showed that it had strong photoluminescence, allowing for adequate contrast for fingerprint examination on problematic and challenging exteriors. The spherical mono-dispersed nanoparticles also improved the powder's transparency and selectivity.³⁷

Nanofibres

Junior et al., prepared dansyl-based fluorescent nanofibers using Polycaprolactone and dansyl cadaverine or dansyl glycine derivative by electrospinning method. The characterization was done by thermal analysis, scanning electron microscope, FTIR, and fluorescence spectroscopy. With 2% fluorophore concentration in dansyl cadaverine or dansyl glycine, a working distance of 12 cm among the syringe tip and collector, and a voltage of 17 kV, the best experimental conditions for homogeneous, even, and bead-free fibre forming of all samples were discovered. Electrospun Polycaprolactone/ dansyl cadaverine and Polycaprolactone / dansyl glycine nanofibers emit large emission bands at 485 and 415 nm, respectively, and are fluorescent. This research provided a simple, low-cost method for producing electrospun fluorescent nanofiber materials for forensic applications such as the production of hidden fingerprints on metallic objects such as cartridge cases, knives etc. As compared to the majority of well-known traditional methods, like Powder dusting and cyanoacrylate fuming, the proposed technique has many benefits over traditional techniques including solvent and raw materials with low-toxicity, easy regulation of polymer film formation, and attainment of evidence containing hidden fingerprints on metallic objects of various sizes and shapes, liable on electrospinning collector settings. As a result, this novel approach enabled the high-definition visualisation of formed hidden fingerprint images, as well as the identification of class characteristics, ridge patterns, and singular points of fingerprints.³⁸

Benzazole dyes have characteristics like high sensitivity, stable and intense photoluminescence

which can enhance the latent fingerprints. Stefani et al. considered benzazole dye to prepare micro-structured fluorescent powder to develop the dormant fingerprints present on various surfaces having different color in background like multi-colored, white, and dark. The fluorescent powders were extremely selective and sensitive which only stuck to fingerprints rather than the whole treated area. Irrespective of the color of the surface, the high fluorescence produced by the powder provided a high disparity with the finger impressions, making them easy to recognize and capture. Silica was used as the matrix in the formulation of powder having a 1:100 and 1:300 mass ratio, having ethanol or aqueous solution underneath encompassing settings. Silica is non-toxic, biodegradable, and environmentally safe in nature. The excited-state intramolecular proton transfer mechanism and the high Stokes change detected for the integrated dyes were responsible for the proposed powders' high chemical and photophysical stability, resulting in a extended shelf lifespan. This too permits for the long-term storage of processed evidence without any deterioration of the exposed fingerprints. ultraviolet-visible absorption and fluorescence emission spectroscopy were used to determine the photophysical properties. Assessments were made with commercially obtainable fluorescent, white, and black powders for various types of surfaces to determine the efficacy of these industrialised residues. When exposed to long wavelengths of ultraviolet light at 365 nm, the created micro-structured powders showed intense visible light emission within the blue-green field, and a pointy distinction with the finger impression deposits was discovered, developed discrete ridge data on all studied exteriors. The method is cost-effective and also a simple technique to develop the hidden fingerprints on various kinds of surfaces with distinct levels of information. This fluorescent powder is versatile in nature and can be used in the forensic examination as a multipurpose choice.³⁹

Numerous fluxes, such as NaCl, NH₄F, and NaBr, were used by Dhanalashmi and her colleagues for their study to synthesise novel BaTiO₃:Eu³⁺ (5 mol percent) nanophosphors through a solution combustion path. The effect of the fluxes on the prepared nanophosphors' physical,

structural, and photoluminescence possessions was thoroughly investigated. The cubic structure of the products is verified by powdered X-ray diffraction outcomes. The synthesized samples were sphere-shaped with accumulation, according to the morphological studies. The addition of fluxes results in a significant increase in the red emission intensity in the photoluminescence study. It was discovered that NH₄F (3 weight%) was an effective flux for lowering the temperature formation, morphology improvement, and increasing the photoluminescence strength by two-fold. The samples' photometric properties were calculated and found to be very similar to commercial BaTiO₃: Eu³⁺ phosphor. The fingerprints that have been visualised show that they were highly sensitive, have good contrast, and have no background interference. The results showed that the optimised sample opened up a new path for the easy visualisation of hidden finger impressions in anti-counterfeiting, forensic sciences applications.⁴⁰

DISCUSSION AND CONCLUSION

Latent finger print development is cornerstone in any criminal investigation. Fingerprints are the crucial evidence for the identification of a suspect or culprit in any crime scene. It identifies the individual as fingerprints are unique; no two individuals share the same fingerprint. However, there is a profusion of fingerprint enhancement techniques for the visualization of hidden finger impressions. Powder method is one of the oldest techniques which are still used to develop the prints at the crime scene but it has its own drawbacks like less sensitivity, background disturbance, interference with cellular material visualization techniques, and might not enhance all the levels of finger impressions. Recently, the use of fluorescent nanomaterials like up conversion nanomaterials

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and quantum dots for the enhancement of latent finger impressions have attracted a lot of attention. Fluorescent nanomaterials for fingerprint development have shown many benefits like low toxicity, high developing contrast and selectivity, and high sensitivity. Rare earth upconversion fluorescent nanomaterials doped with rare earth elements can enhance the dormant finger impressions and emits the brightest upconversion fluorescence. On the other hand, a conjugated polymer based fluorescent material also develop a detailed image of finger impression that can be cost effective and having low toxicity with high emission of fluorescence. Similarly, quantum dots showed a higher sensitivity and image excellence when developing dormant fingerprints from level one to three. Therefore, fluorescence-based nanomaterials method developed here allows for successful imaging of hidden finger impressions on a variety of absorbent, non-absorbent, and semi-absorbent materials with high characterisation of first to third level detail, which is in line with the forensic science standard for finger impression identification. **IJFMP**

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