Chapter 3
Latent Fingerprint Development from Magnetic Nanoparticles

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Introduction

With the advancement in various fields of forensic science, many new research articles are published making latent fingerprints visible. Fingerprints being unique has the potential in many a case and their development has become a top priority task in forensic science. Developing fingerprints with powders for their detection, imaging, and identification has become the most common technique in crime investigation [1, 2]. Dusting methods are majorly used by policemen in screening the crime scene for developing the latent fingerprint. Some trouble can also occur like the physical and chemical nature of the surface, fingerprint donor, contaminants present, environmental conditions, and age of latent fingerprint [3–5]. Various literatures are published discussing chemical and physical techniques to overcome these troubles in visualizing the latent fingerprints on various surfaces. There are conventional methods which get adhere to the sticky secretion by the pores present on ridges of fingerprints on the various surface. While the chemical substances interact with the organic or inorganic residue present on the surface due to the impression left by fingerprint [6–12].

Due to various challenges, be that stickiness on surface or lifting from the surfaces it has been quite a challenging task, some methods are discussed in different literature [3, 13–19]. Here in the situation, MNPs have the advantage of lifting latent fingerprints (LFPs) easily by use of ordinary or permanent magnets and also have

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K. K. Awasthi et al. (eds.), *Friction Ridge Analysis*, Materials Horizons: From Nature to Nanomaterials, https://doi.org/10.1007/978-981-99-4028-8_3

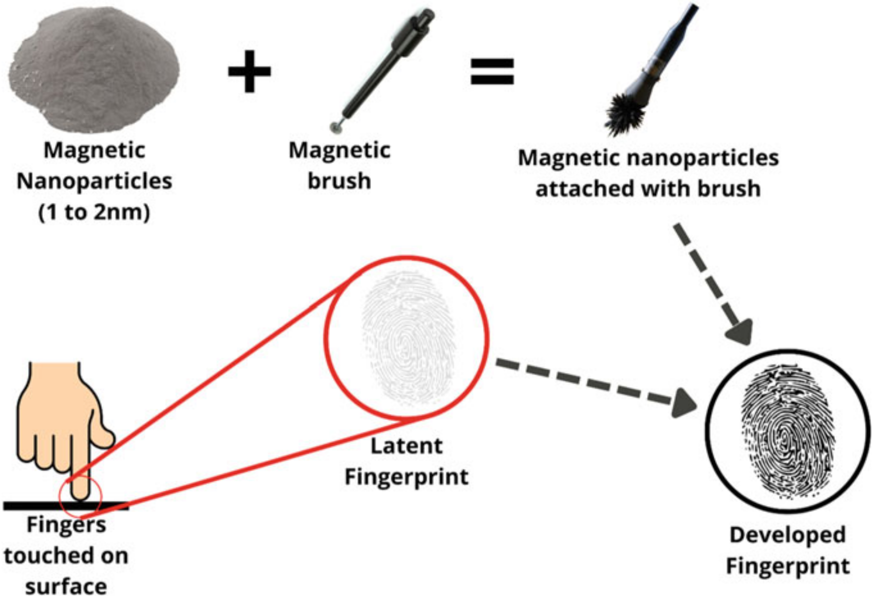
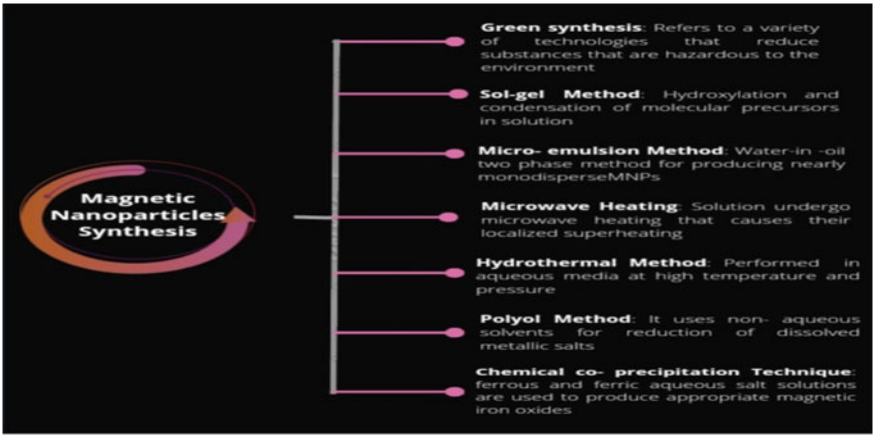


Fig. 3.1 An image showing development of latent fingerprint with the help magnetic nanoparticle

high visualizing power. In the technology of developing LFPs by means of magnetic nanoparticle powder, here the powder in dry form adheres to organic or inorganic substances present in the fingerprint present on the surface. It is very vital to select an MNP with respect to the surface, particle, and the type of remaining fingerprints. Figure 3.1 shows the development of LFPs on the surface using a magnetic brush and MNPs.

The finer magnetic powder has the ability to adhere more to organic or inorganic substances than the coarse one [1]. Fingerprints on the surface will have a complex mixture of natural organic and inorganic particles, so lipophilicity and size of the particle are very crucial parameters to get a high visualization of latent fingerprints on the surface. MNPs such as Fe_3O_4 and also $Fe_3O_4@SiO_2$ have polar nature because of their negative charge and the presence of –OH formulates hydrogen bonds with polar compounds such as moisture as well as Vander Waals dispersion forces and attraction due to dipole–dipole [9, 20–22]. In order to achieve better results during the development of fingerprints, there is a need to create lipophilic interaction between the residue and dusting agent [3]. For creating MNPs more attention should be given to their lipophilicity which can solve the above-mentioned problem of lipophilic interaction and efficiency of the powder. Lipophilic interactions with respect to MNPs are referred to as the ability of the MNPs to attract the residue present in the fingerprint such as fats, oil, lipid, and non-polar substances.

With respect to other used methods or techniques for the development of LFPs, MNPs have few advantages over them. MNPs have strong magnetism, with the help



Green synthesis: Refers to a variety of technologies that reduce substances that are hazardous to the environment

Sol-gel Method: Hydroxylation and condensation of molecular precursors in solution

Micro- emulsion Method: Water-in -oil two phase method for producing nearly monodisperseMNPs

Microwave Heating: Solution undergo microwave heating that causes their localized superheating

Hydrothermal Method: Performed in aqueous media at high temperature and pressure

Polyol Method: It uses non- aqueous solvents for reduction of dissolved metallic salts

Chemical co- precipitation Technique: ferrous and ferric aqueous salt solutions are used to produce appropriate magnetic iron oxides

Fig. 3.2 The figure shows the different synthesis methods of the magnetic nanoparticle

of this property we can recover and recycle the used powder. With the help of a magnetic brush and an external magnetic field, the excess powder can be recycled and utilized and aerosol formation due to dispersion in the air of these MNPs can be prevented as it can damage the health of a person who is developing the LFPs. MNPs has also the property of high sensitivity, as the size of MNPs is small, they can reflect very fine ridge details by adhering to the moisture resent on the fingerprint due to sweat pores. A very small amount of MNPs used can give the development of LFPs. With advantage MNPs also has some disadvantages as for producing a high cost is required and there is a limitation for scale-up production and the mobility depends on the environment compatibilities [23]. Figure 3.2 discusses the different methods which can be used for the synthesis of MNPs.

Magnetic Nanoparticles Synthesis

Diacetylene (DA) Powder

For the synthesis of Diacetylene, a mixture of $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ was added to deionized water. The mixture was heated at the temperature of 78 °C and to maintain the pH of the mixture addition of dilute aqueous ammonia hydroxide was done. For 24 h the sample solution was heated at the same temperature and once the heating is done, filtration was done for the Fe_3O_4 particle. Fe_3O_4 particles were collected and then again washed with deionized water and then dried in the vacuum condition so that 53% of the desired magnetite nanoparticles is afforded. Then for the preparation of Diacetylene—Magnetite Composites, a crucible was taken, and in that mixture of 10,12-pentacosadiynoic acid (1.0 g) and magnetic nanoparticles (500 mg) in tetrahydrofuran (10 mL) was gently ground till the evaporation of solvents is completed.

The fingerprint was successfully developed using the DA powder over the solid substrate. The immobilization of DA powder was achieved by moving the magnet under the solid substrate. The excess powder was removed using an air blower. To irradiate the Diacetylene-immobilized image a UV light is used and heat treatment was provided at last to convert the blue phase to the red phase image. The most perceptible image was formed when the weight ratio of Pentacosadiynoic acid (PCDA) to MNP was 20:1 because the red color shows more fluorescent, and a well-developed ridge was clearly visible under a fluorescence microscope. It was observed that the sebaceous lipid-like DA molecules facilitate the immobilization of the DA on fingerprint ridge structures [24].

Fe_3O_4 GSH-Pt NCs

The co-precipitation method for the synthesis of Fe_3O_4 was used. The mixture of NaOH and KNO_3 was added to H_2O. This solution was added to Fe_3O_4 solution and heated at 25 °C for half an Hour. After that centrifuge at 10,000 rpm for 15 min was done then washing with deionized water was done thrice. Polyethyleneimine (PEI) solution was ultrasound for 15 min and then the Fe_3O_4 was added to that and heated at 80 °C. Then microwave-irradiated in the microwave and then ultracentrifuged. With centrifugation, the precipitate is washed with deionized water to obtain PEI- Fe_3O_4 solution. To fabricate glutathione (GSH)-Pt NCs, GSH was added to H_2PtCl_4 with continuous and fast stirring. When the mixture was mixed evenly then it was ultrasound and then heated in the microwave oven, this step was repeated to get GSH-Pt NCs. For fabrication of Fe_3O_4 on GSH-Pt NCs powder, the solution created above was mixed evenly at room temperature, the + ve and -ve charged solution experienced electrostatic adsorption and Fe_3O_4 GSH-Pt NCs core–shell microspheres were obtained.

Fingerprints were developed on a dark wood desktop. The Fe_3O_4 GSH-Pt NCs powder was applied with the help of a brush in a clockwise direction alongside ridges. A successful fluorescent image was obtained by a self-assembled development observation system [25].

Lipophilic Fe_3O_4@SiO_2@MeMFNPs

For synthesis of Fe_3O_4 magnetic nanoparticles, a mixture in deionized water under the nitrogen atmosphere and mechanical stirring of ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and ferric chloride hexahydrate $FeCl_3{\cdot}6H_20$. And for adjusting the pH to 9–11, an aqueous solution of NH3 was added and stirring was provided. After that filtrate was washed with distilled water and black precipitate of Fe_3O_4

was collected with the help of external magnet. Then for preparation of silica-coated Fe_3O_4 MNPs, an ultrasonic premixing of black precipitate of Fe_3O_4 in ethanol. After that aqueous NH_3 and TEOS were added, then mechanical stirring was provided and with the help of external magnet, a silica-coated Fe_3O_4 precipitate was collected and dried under the vacuum at room temperature. Then a lipophilic nature was provided to silica-coated Fe_3O_4 with methyl moieties based grafting of precursor trimethoxymethylsilane (TMMS). In a dry toluene which had silica-coated magnetic nanoparticle, TMMS was added. The mixture formed was stirred for 24 h and the solution was washed many times with toluene and ethanol, and in vacuum condition powder was dried and lipophilic magnetic nanoparticles were formed.

The fingerprints were developed and the magnetic property of the powder was helpful for removing the excess powder present on the LFP. There was a decrease in magnetic saturation due to the presence of silica shell coated on magnetic particles. But saturation was sufficient for removing the physical magnet. The formation of LFPs was due to physico-chemical process between the skin and surface. Physical property of powder and oily component helps in adhesion, in that way the silica-coated MNPs were designed to create lipophilic and microscopic interaction with oil and greasy molecule. And these powders showed a good contrast and clarity in LFPs. With the help of tape and gelatin film, and photographic method the LFPs were recorded. The prints were successfully collected from porous surface be that wall, paper sheet, medium-density fibreboard, and nonporous surfaces including plastic wall, water glass, and door handle made up of metal [20].

P-MNP@Ag Magnetic Nanoparticle

For synthesis of nanosilver, $AgNO_3$ needs to be added in water and heated, followed by the addition of sodium citrate. A continuous stirring needs to be provided by mechanical stirrer and then cooled at room temperature. For synthesis of $Fe_3O_4.FeCl_3.6H_2O$ in a flask, $Fe_3O_4.4H_2O$ and distilled water were added and to maintain pH ammonia was added and then a gel of black color appeared in large amount. Solution was heated and continuous stirring was given and the black color product obtained due to centrifuge was washed with the ethanol. And then Fe_3O_4 was dried under vacuum conditions at room temperature. Then for the final synthesis of S-MNP, Fe_3O_4 and distilled water were added and ultrasonicated, and to that 3-mercaptopropyl triethoxysilane (MPTES) with ethanol and acetate was added and on ice bath it was ultrasonicated. Then to Fe_3O_4 and ultra-sonicated water the above made solution was made and after that centrifugation was done, the precipitate was washed with ethanol and then dried under vacuum condition and ground to fine particles, and stored. To make P-MNP Ag a facile coprecipitation was formed, firstly synthesis of P-MNP-0.13. $NH_3.H_20$ was taken in flask and to that MPTES was added very carefully and the striation was provided. In the flask $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were taken and distilled water was added and stirred. Then the hydrolyzed MPTES was added into flask to make pH to 9, striation was provided and black precipitate opted out and they were washed with ethanol. They were collected and dried at room temperature, and were ground to fine particles. And like this the amount of MPTES was changed and different magnetic nanoparticles were synthesized: P-MNP-0.043, P-MNP-0.13, PMNP-0.36, and P-MNP-1.08. Then synthesis of P-MNP Ag. P-MNP-0.13 was dispersed in distilled water and stirred and then carefully drops of nano silver were added and then ultra-sonicated for 2 h. Once reaction is quenched it was centrifuged and precipitate was washed with ethanol and collected and dried in vacuum, and then the final product was converted to fine particles.

Fingerprints were developed on porous surfaces such as paper, artificial leather, filter paper, weighing paper, and non-permeable objects such as metal doorknobs, railings, plastic bottles, and plastic wash basin. P-MNP Ag has excellent development effects on plastic and paper. Due to smooth texture of P-MNP Ag than of S-MNP Ag, it was able to develop LFP on plastic and leather. P-MNP Ag showed very less background interference, and was highly sensitive and was able to show very fine secondary details of the LFPs on many of the surfaces with less time taken for development [26].

Fe_3O_4 Ag Nanoeggs

For the synthesis of Fe_3O_4 nanoparticles coprecipitation was used. Coprecipitation of ferric and ferrous chloride was added into the NaOH and stirring was provided. Then cooling was done in an atmosphere of nitrogen and black product which resulted was washed with ethanol, then fabrication of APTES-modified Fe_3O_4 nanocomposites was done by keeping Fe_3O_4 nanoparticle in ethanol and then APTES mixture along with CH_3COOH or $NH_3 \cdot H_2O$ was added and mixture reacted vigorously under water bath. Precipitate was filtered and separated by permanent magnet and washing was done using ethanol. Then fabrication of Fe_3O_4 Ag nanoeggs was done. APTES-modified Fe_3O_4 nanoparticles were mixed with Ag nanoparticles and were kept for adsorption to take place. Excess amount of Ag was removed using magnet and after that particles were dispersed in ethanol. A shell of Ag-modified Fe_3O_4 magnetic nanocomposites was formed by reducing aliquots of AgNO3 with NaBH4 in magnetic separation and dissolved in distilled water.

The fingerprints were developed using adhering property of powder with moisture and oily components, and excessive amount of powder was removed by dusting or gently blowing on the surface. These modified Ag Fe_3O_4 nanoeggs were strongly attached to magnetic brush. They were able to produce less background development due to smooth surface of the Ag and that gave a good contrast between the LFPs and surface. Fe_3O_4 Ag nanoeggs powder was synthesized in different pH and it was found that fingerprints which were developed using the higher pH nanoeggs powder showed more intensity of powder and maximum background development was observed due to the bigger size of Fe_3O_4 Ag nanoeggs. Fe_3O_4@Ag nanoeggs showed excellent ridge details with minimal background staining on glass, porcelain enamel, polyethylene pieces, and paper surfaces [27].

Conclusion

To develop latent fingerprint adherence and reaction are two properties for their development. So these magnetic nanoparticles get adhered to the moisture and oily substances present due to the sweat spores present on the fingers. The magnetic particle due to their fine texture and surface gets smoothly adhered to the surface and decreases the background development and gives high contrast development of latent fingerprints. And the excessive amount of powder can be recovered from the development area with the help of external magnet and like other nanoparticle hazardous to the person who is developing those fingerprints, these magnetic nanoparticles doesn't show such threat. These magnetic nanoparticles can be tuned or modified according to the concern of their response toward magnetic field. But the drawback is the cost of production of very minute quantity is very high. These magnetic nanoparticles can show very high contrast of latent fingerprint. In the field of forensic science to develop latent fingerprint, magnetic nanoparticle can play a crucial role, due to their property of producing high contrasting images and decreasing the background noise. Magnetic powder sowed its development on all kinds of surfaces, according to the type of surface the MNPs powder can be used and LFPs can be developed. Fingerprints on the surface will have a complex mixture of natural organic and inorganic particles, so lipophilicity and size of the particle are very crucial parameters to get a high visualization of latent fingerprints on the surface.

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