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$CoFe_2O_4$ Based Black Magnetic Fingerprint Powder: Development, Analysis and Applications of Nanoparticles in Decipherment of Latent Fingerprints

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Abstract

Herein, we report the synthesis of magnetic cobalt ferrite (CFO) nanoparticles (NPs), to study its application for the development of latent fingerprints using rapid and cost-effective combustion method. X-ray diffractometer (XRD) has been utilized for the structural analysis, which confirmed the pure phase of synthesized nanoparticles. The CFO NPs were utilized in order to decipher the latent fingerprints over a non-porous surface. Developed fingerprints were observed under a stereomicroscope and a large number of pores could be identified and differentiated as open or closed pores, and the average pore size has been calculated. All the obtained results were compared to the results obtained using commercial black magnetic latent fingerprint powder, which established the superiority of synthesized CFO nanoparticles. Current study may pave the path for the development of a potential black magnetic fingerprint powder, which can effectively reveal the fine features of latent fingerprints after development.

Keywords: *Forensic Science, Latent Fingerprints, Nanoparticles, Cost Effective, Cobalt Ferrite*

1. Introduction

Forensic Science is an applied science which aids the law by providing and analyzing scientific evidences found at the scene of crime [1]. According to the Locard's principle of exchange, any object, person or place that comes into contact with another object, person or place, takes something from the other and leaves some part of itself behind [2]. This law forms the basis on which scientific evidence gets its value, and is the reason why evidence is collected, to link a perpetrator to a crime. These evidences may include biological and chemical evidences, trace evidences and various impression evidences such as fingerprints and tire marks [3]. Among these evidences, the ones most commonly found at a crime scene are fingerprint impressions [4].

Fingerprints are a crucial type of physical evidence which help in the identification of individuals associated with a crime, may it be a suspect or a victim [5]. It helps to form an evidential link between the individuals and their presence or absence at the scene of crime. A fingerprint is an impression of the friction ridge skin formed on a surface when it comes in contact with the finger of a person. The three types of fingerprint impressions are (i) latent fingerprints, (ii) patent fingerprints [6], and (iii) plastic fingerprints [7]. Unlike the other two, latent fingerprints are not generally visible to the naked eyes, and their formation can be attributed to the deposition of sweat secreted by the sweat pores present in the ridges onto the surface [8].

Numerous physical techniques and chemical techniques have been employed for latent fingerprint development on non-porous as well as porous surfaces [9]. Each of these tests gives a developed image of the latent fingerprint by reacting with specific components of sweat present in the latent fingerprint impression. Powder method is a physical technique ideal for developing latent fingerprints on non-porous surfaces and is widely utilized during crime scene investigations due to the simplicity of the method [10]. The fingerprint powder (FPP) is durable, easy to store and transport. Fingerprint powder is lightly dusted using a fingerprint brush on a surface that is suspected to have latent fingerprints on it [11]. The FPP adheres to the latent fingerprint's moisture content and the fingerprint becomes visible as it gets developed. Thereafter the developed fingerprints can be collected as evidence by photography [12] and tape-lifting [13]. The FPP can be synthesized using different methods to attain required surface, structural, optical, morphological and magnetic properties.

In recent years, nanomaterials have continued to gain the interest of the scientific community. This is due to the ability to control their size (less than 100 nm), their shape and the ability to tune their properties based on the required application [14]. They can also be modified to have various morphologies and dimensions, such as nanoparticles, nanorods [15], quantum dots [16] and nano-sheets [17] by employing synthesis methods including hydrothermal [18], sol gel [19], solvothermal [20], and chemical ablation method [21]. Spinel ferrite nanoparticles with the chemical formula MFe_2O_4 have gained popularity in the scientific community. In spinel ferrites, the metal cations, M (Mg^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, etc.) and Fe^{3+} occupy tetrahedral and octahedral sites respectively [22]. They are cost efficient, which makes them an attractive option for large scale manufacturing.

$CoFe_2O_4$, also known as Cobalt Ferrite (CFO) is one such spinel ferrite with an inverse spinel structure [23]. It is known for its magnetic, electrical, catalytic and optical properties. It has been synthesized by various methods including co-precipitation method [24], supercritical hypothermal synthesis [25], precipitation method [26], sol-gel auto-combustion [27], and continuous hydrothermal synthesis [28]. CFO nanoparticles have been studied for magnetic hyperthermia [29], targeted drug delivery [30], photoelectrochemical [31], microwave [32] and nanogenerator [33] applications. It is apparent that cobalt ferrites, and spinel ferrites in general have proven to be important in several fields of applied sciences. However, few have looked into its prospective applications in the field of forensic science [34]. CFO can be considered a promising candidate for black fingerprint powder due to their additional magnetic properties.

In this paper, the structural properties of CFO nanoparticles synthesized by combustion method have been thoroughly studied, to further explore its potential application in latent fingerprint development and examination. The prepared NPs were studied using XRD and the developed fingerprints were examined using a stereomicroscope for pore-based study.

2. Synthesis

Using combustion method we have synthesized cobalt ferrite nanoparticles, as this method is ideal for bulk synthesis, cost effective and less time consuming. For this cobalt nitrate hexahydrate

($Co(NO_3)_2.6H_2O$)(0.0103 mol), ferric(III) nitrate nonahydrate ($Fe(NO_3)3.9H_2O$)(0.0198 mol) and glycine ($C_2H_5NO_2$)(0.5328 mol) were mixed in 100 ml of water. This mixture was placed in an ultra-sonicator for 5 mins creating a suspension, which was then stirred using a hot plate magnetic stirrer. The semi solid product was collected in a crucible and annealed in a laboratory furnace at 650 ºC for 5 hrs and then cooled down naturally. It was grinded to attain a fine powder, which would further help in the washing process that followed. The resultant product was heated in the Hot Air Oven and then grinded to obtain CFO nanoparticles. Fig. 1 depicts the process of synthesis of CFO nanoparticles by combustion method.

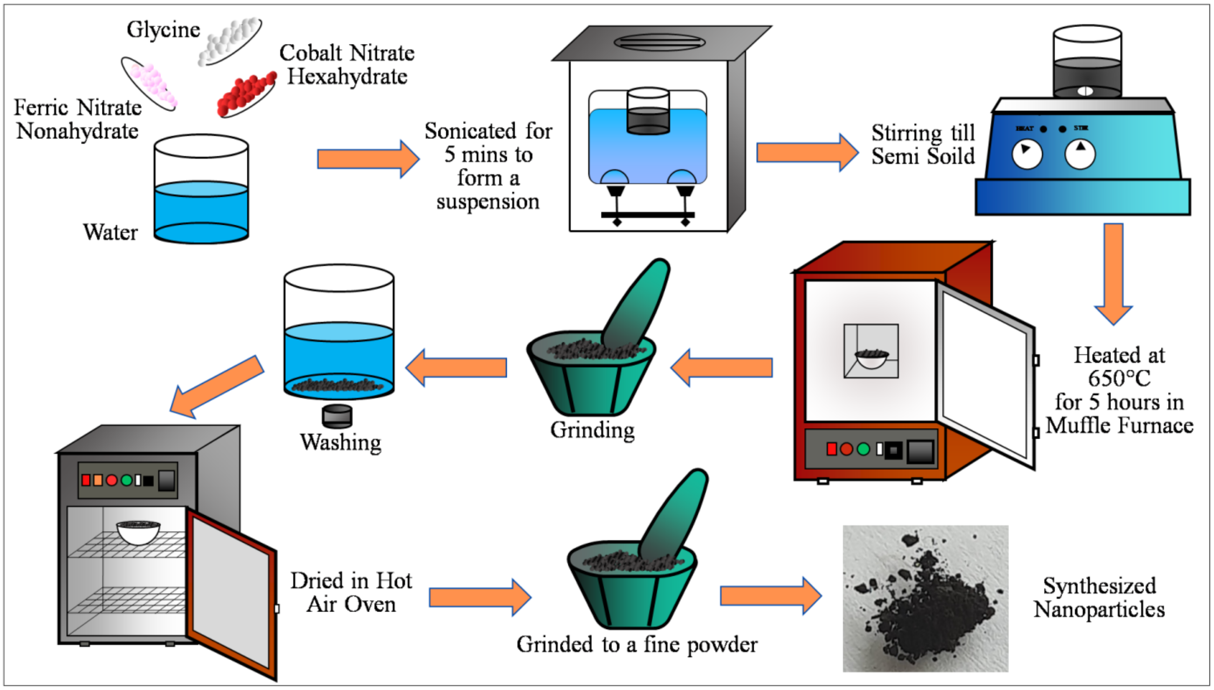

Figure 1. Schematic representation of cobalt ferrite nanoparticles'synthesis.

3. Results and Discussion

3.1 X-Ray Diffraction Studies of Synthesized Nanoparticles: The XRD pattern of the CFO NPs synthesized by combustion method is shown in Fig. 2. The XRD pattern was obtained using Rigaku Ultima IV equipped with X-ray radiation - Cu Kα (wavelength 1.542 Å).

Table 1. Peak positions in 2θ (in degrees) along with their corresponding miller's indices and d-spacing.

hkl	2θ (in degrees)	~d-spacing of (Å)	Reported d-spacing (Å) [36]
111	18.4	4.8	4.8
220	30.3	2.9	2.9
311	35.7	2.5	2.5
400	43.4	2.0	2.0
422	53.7	1.7	1.7
511	57.4	1.6	1.6

The XRD peaks were taken for a range from 10º to 60º of 2θ. The peak positions have been listed in Table 1 along with their corresponding Miller Indices (hkl) and inter planar spacing (d-spacing). The inter planar spacing was calculated using the equation given by Bragg [35];

$$n\lambda = 2dsin\theta \tag{1}$$

here "n" be the order of diffraction, "λ" be the incident wavelength (X-Ray beam), "d" is the inter planar spacing and "θ" is the Bragg's angle. All the Bragg reflections presented in Fig. 2. correspond to the spinel cubic phase of CFO nanoparticles with the absence of any secondary phase, confirming the purity of phase formation.

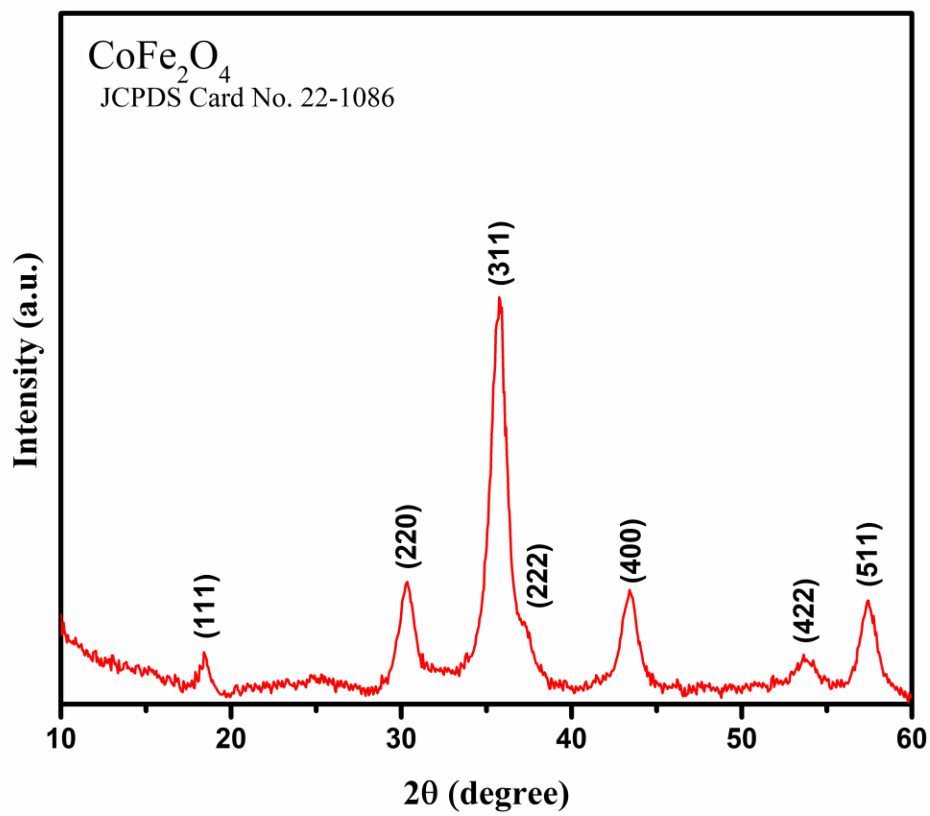

Figure 2. XRD pattern for synthesized cobalt ferrite nanoparticles.

The average crystallite size (D) of the synthesized CFO NPs was calculated using Scherrer equation [37];

$$D = \frac{k\lambda}{\beta cos\theta} \tag{2}$$

here "k" is the Scherrer constant and "β" is the full width half maximum. The D value of the synthesized CFO nanoparticles' was found to be ~8nm, which is equivalent to previously reported values for similar broadening of CFO XRD data [38].

3.2 Development and Tape-Lifting of Latent Fingerprints: For examining the potential of the synthesized powder for latent fingerprint development, latent fingerprint impressions were taken on a non-porous surface with a light background (glass, white glossy paper, whiteboard, white painted metallic surface) and under similar conditions. The light background is used due to the black colour of CFO nanoparticles that provide a good contrast against the surface. The fingerprint impressions were then developed with the CFO nanoparticles by powder brush method using a standard fingerprint brush. At the same time, fingerprints were developed using commercial black magnetic latent fingerprint powder (Technomaxx Forensics Pvt. Ltd.) for comparison with the synthesized sample. The ease of application onto the surface, the quality of contrast provided by the developed fingerprint against the light surface, the quality of the developed fingerprint after tape-lifting, the ease of identifying pores and the number of pores that could be identified were taken into account for comparison. The ease of application for both the fingerprint powders was identical.

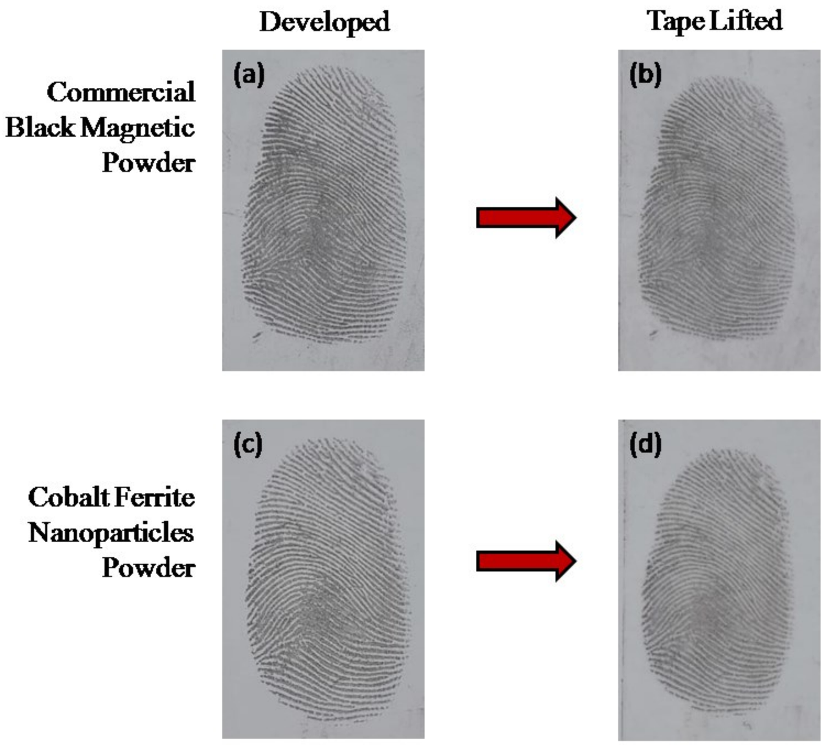

Figure 3. **(a)** Developed latent fingerprint on a white painted metallic surface, and **(b)** tape-lifted fingerprint onto a standard fingerprint card with commercial black magnetic powder. **(c)** Developed latent fingerprint on white painted metallic surface, and **(d)** tape-lifted fingerprint onto a standard fingerprint card with cobalt ferrite nanoparticles.

The developed fingerprints for both samples showed a similar quality of ridges with a uniform and consistent spread of the powder. Due to the high contrast, the ridge characteristics were easy to examine. During the development of the latent fingerprints, it was noted that the CFO nanoparticles quickly adhered to the fingerprint and there was no smudging on the rest of the surface. On the other hand, it was observed that some amount of commercial black magnetic powder seemed to smudge the surface surrounding the fingerprint. When the developed fingerprints were lifted using a fingerprint lifting tape onto a fingerprint card, they remained unvaried and accurately retained most of their physical features.

Fig. 3 (a) depicts a latent fingerprint developed using commercial black magnetic powder, and (b) depicts the fingerprint after being tape-lifted onto a standard fingerprint card. While (c) and (d) depict a latent fingerprint after being developed and after being tape-lifted using CFO nanoparticles respectively. The comparison of the developed and tape lifted samples was done for 20 different sets of 2 latent fingerprints each, with one fingerprint developed using CFO nanoparticles and the other developed using commercial black magnetic powder on a white painted metallic surface.

There exist three levels of fingerprint classification. The first level is the classification of pattern type and the second level of classification deals with ridge characteristics. The third level of classification, that is poroscopy, is the most difficult one, as it involves the study of pores visible in the fingerprint impressions [39]. The pores can be closed pores, which are completely surrounded by the ridge in which it is present, or open pores [40], which appear to be partially outside the ridge in which it is present. It is quite taxing to find pores in latent fingerprints developed by powder method. Please note that, commercially available latent fingerprint powders have typical particle size in micrometres and have low surface to volume ratio. On the other hand, nanoparticles, because of their smaller size, can give detailed visualization of developed latent fingerprints if used as a fingerprint powder [41].

Latent fingerprints were collected on glass slides under similar conditions and developed using either of the two powders. These were examined under a stereomicroscope to examine the pores and to calculate their average pore size [42]. Fig. 4 depicts the visualisation of pores under a stereomicroscope for latent fingerprints developed using (a) CFO nanoparticles and (b) commercial black magnetic powder. 30 different sets of 2 latent fingerprints each, one developed using CFO nanoparticles and the other using commercial black magnetic powder were used for comparison to ensure that the synthesized powder was truly helping to visualise pores and to ensure that faulty method of application did not affect the visualisation of pores. The pores appeared to be more prominent in the fingerprints developed with CFO nanoparticles and a larger number of them could be identified. Open and closed pores could also be differentiated effortlessly. Pore sizes were measured using Radical ProCAM software. The average pore size was calculated by measuring the diameters of closed pores and, for open pores, the distance between opposite ends of the pore was measured. The average value was found to be ~232µm for a total of 25 pores.

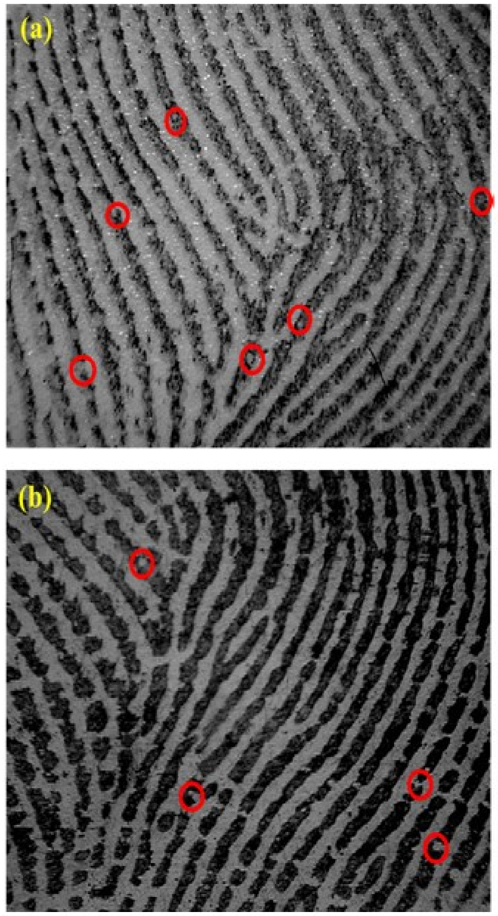

Figure 4. **(a)** Visualization of pores using synthesized cobalt ferrite nanoparticles, and **(b)** commercial black magnetic powder on a glass slide as observed under a stereomicroscope.

4. Conclusion

We have synthesized CFO nanoparticles using combustion method. The CFO nanoparticles were characterized using XRD and it was found that the synthesized particles were pure in phase without any noticeable impurity. The crystallite size of the nanoparticles was calculated to be ~8nm. The fingerprints developed using CFO nanoparticles on a non-porous surface using a standard fingerprinting brush provided the best contrast on light background surfaces. Clear ridge patterns with well-defined boundaries and no smudging were observed. These properties were retained even after tape lifting. Pore studies of the developed fingerprints using a stereomicroscope revealed that a number of pores could be identified. The pores could easily be differentiated into open or closed pores. The average pore size was calculated to be ~232μm. Upon comparison of the results obtained using CFO nanoparticles powder with those obtained using commercial black magnetic powder, it was found that CFO nanoparticles caused less smudging on the surface surrounding the latent fingerprint and a larger number of pores could be identified and differentiated with more clarity due to the small crystallite size of the CFO NPs making it a potential candidate for the decipherment of latent fingerprints. Although fragmentation of developed ridges in latent fingerprints developed using CFO nanoparticles is a possible limitation for its use, innovation in latent fingerprint development using nanoparticles has a bright future. There is room for improvement in the clarity of visualisation of developed pores. Research on nanoparticle based latent fingerprint development powder for different coloured backgrounds, porous and non-porous surfaces is promising.

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All the authors listed below have made significant contributions to the creation of this manuscript and were responsible for all aspects of the work. Each author played a role in the below mentioned aspects of the research and manuscript preparation:

- **Conceptualization:** VNH, SM
- **Methodology:** VNH, SM
- **Investigation:** VNH, ASN, DM, RK, SM
- **Formal Analysis:** VNH, ASN, DM, SM
- **Data Curation:** VNH, ASN, DM
- **Writing - Original Draft:** VNH, ASN, SM
- **Writing - Review & Editing:** VNH, ASN, SM
- **Visualization:** VNH, SM
- **Supervision:** SM

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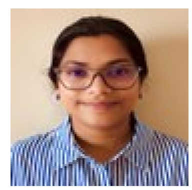

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