



Extent of Nanotechnology in Forensic Science

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ABSTRACT

Nanotechnology has a tremendous potential in the field of science and technology. It has been used and applied in various forms for the enhancement of already existing materials, and termed as Nanomaterials. This includes use of Nanomaterials in electronics, engineering, physical sciences, materials sciences, biomedical sciences, forensic science and many more. Most important advantage of nanotechnology in forensic science has been in revealing latent clues at the scene of crime, which can prove to be imperative in giving justice. The latest developments in the advanced analytical analysis techniques have incorporated nanotechnology in forensic investigations like never before. In this chapter, we will focus on the use of nanomaterials and nanotechnology in the field of forensic science and how it has benefited the criminal investigation, evidence examination and facilitating their admissibility in the court of law.

Keywords: Nanomaterials, nanotechnology, forensic, science, law, crime, analytical techniques, investigations, evidence.

INTRODUCTION

Nanotechnology maybe cumulatively defined as the study, design, creation, synthesis, manipulation, application of functional material devices and systems through control of matter at a nanometer scale^[1]. The word “nano” is derived from the greek word “dwarf”. A nanostructure is an object described between the size of 1-100 nm. The materials at nanometer scale possess different and enhanced properties compared with the same material at larger size, and this makes them superior than other^[2]. The fundamental idea regarding the concept of nanotechnology was given by Dr. Richard Feynman in 1980s^[1].

Nanotechnology can be applied to forensic science in two ways; the first method is the detection and analysis of samples in a nanoscale. The second method is the assistance of nanomaterials with novel properties, in the collection and detection of evidences^[1].The implementation of nanotechnology in forensic science involves the development of reactive materials, microchip technology, nanomanipulators, nanoimaging tools, for visualization. Nanotechnology alone or in combination with other technologies have significant application in security, drug screening, explosive and latent fingerprint detection, the analysis of questioned document and DNA analysis^[3]. The evolution of nanosensors and nano devices for identifying anonymous evidence is one of the novel application of nanoforensics.

1. Nanotechnology and fingerprints detection

Finger prints formed by the frictional ridge skin at the end of our fingers giving a unique pattern of ridges and valleys to each individual. They have gained utmost importance in forensics because their pattern which is unique to each individual and doesn't change throughout a person's life, even identical twins also has different fingerprints^[2]. The development of latent fingerprints by utilizing nano techniques possess superior properties such as enhanced selectivity, improved contrast with the background, and increased sensitivity. The different types of nanoparticles and their applications in the identification of latent fingerprints are discussed in the following sections:

Metallic silver nanoparticles have been used as a reagent in the silver physical developer (Ag-PD) method since 1970 for the visualization of latent fingerprints on porous paper surfaces. The silver nanoparticles (1–200 nm) formed during the oxidation – reduction couple reaction interact with the organic constituents of the fingerprint residue due to the electrostatic force of attraction and enable the visualization of the impression as a dark gray or black silver image on the paper surface. The print bearing surface should undergo acid pre-treatment to remove CaCO₃ filler if any present. The gold nanoparticles stabilized with citrate ion were applied on the fingerprint before the treatment with Ag-PD solution for the visibility enhancement. Gold nanoparticles (AuNPs) play a significant role in the development of latent fingerprints because of their inert nature, high selectivity and sensitivity. Colloidal gold (Au) of particle size 14 nm or 30 nm in diameter, at sufficiently low pH serves the same purpose^[2, 4-7].

Functionalized colloidal gold with long chain hydrophobic molecule (octadecanethiol) in petroleum ether carrier is utilized for the fingerprint development in both porous and non porous surfaces^[4,8].

The amine functionalized Europium oxide nanoparticles targets the carboxylic acid functionalities of fingerprint constituents. It is applied using SPR technique with an incubation process, followed by photoluminescent detection^[9]. Al₂O₃:Eu³⁺ can serve as the best option for fingerprint development in comparison with ordinary luminescent powders owing to its intense luminescence property^[7]. CdS nanocrystals capped with dioctyl sulfosuccinate in heptanes/ mixture of hexanes develops fingerprint on soft drink can and aluminium foil that are previously fumed with cyanoacrylate ester^[1,3,9]. CdSe ZnS-capped, alongwith ZnS nanocrystals can be covalently bound to amino acid components of fingerprint residue on non porous surfaces and the developed prints are stabilized by octadecaneamine^[4,5,9].

CdS luminescent quantum dots functionalised generation of four starburst dendrimers is also utilized for latent fingerprint development. Metallic oxide nanoparticles such as TiO₂, ZnO, FeO black powder, ZnO –SiO₂ nanopowders and metal sulphide nano powders can be used for the development of latent fingerprint^[3,6,9]. The nanoscale infrared luminescent Egyptian blue pigment particles coated with centrimonium bromide providing lipophilic surfaces are used for the detection of aged latent fingerprints on model surfaces^[15]. Worley and coworkers at Los Alamos National Laboratory performed the latent fingerprint images generation by the non destructive Micro-X ray Fluorescence (MXRF) technique. The Inorganic elements present in the fingerprint residue is detected for imaging purposes^[1,3]. Along with the commonly used physical, chemical methods of development of latent fingerprints, the advanced techniques like Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Desorption Electrospray Ionization Mass Spectrometry (DESIMS), ink-jet-printed array, powdering method- most commonly used (magnetic powder, aluminum flake powder, luminescent powder and iron flake powder), chromatography, Surface Assisted Laser Desorption/ Ionization (SALDI) coupled with mass spectroscopy, Matrix Assisted Laser Desorption/ Ionization mass spectroscopy (MALDI), Raman spectroscopy, Infrared spectroscopy, including acid dyes, cyanoacrylate fuming (CA), and the evaporation of metals such as gold, zinc, and silver can also be utilised for fingerprint visualization purpose^[2].

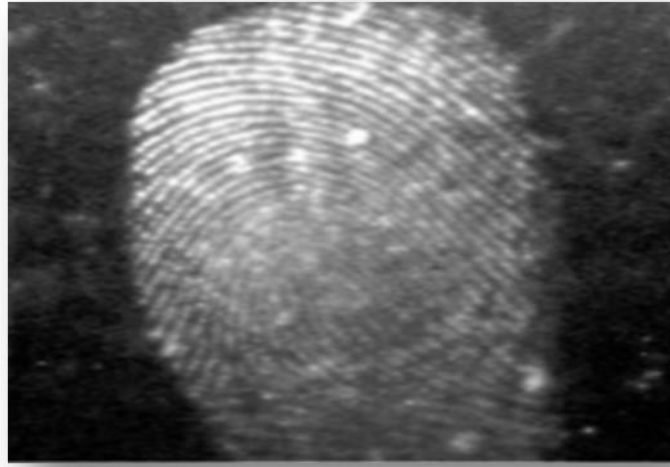


Fig 1:-Ten-day-old fingerprint on glass surface developed by using ZnO nano-powder. Illumination 350-nm, detection 570-nm long-pass filter. [

Credits: reproduced with permission from Springer Nature, J Mater Sci, An evaluation of nanostructured zinc oxide as a fluorescent powder for fingerprint detection, Choi MJ, McBean KE, Ng PHR, McDonagh AM Andrew, Maynard PJ, Lennard C, Roux C, 2008. 43,732–737, Copyright (2019).]^[7].

2. Nanotechnology and drug detection.

Due to the smaller size, nanoparticles can come in contact with larger surface area and thus can potentially react with more active sites. Different toxic substances of evidential value can be detected and quantified from samples such as blood, saliva, hair, vitreous humour, skeletal remains and even from fingerprint samples. Forensic drug test can be generally carried out in 2 ways i.e. screening and confirmation. Nanosensors provide excellent signal amplification for chemical and biological sensing due to their unique optical, electrical, and thermal properties as well as catalytic properties. Molecular receptors of a nanosensor serve as templates for the material to be detected. Several materials can be used as receptors^[1,5,10]. Au nanoparticles functionalized with anticotinine, an antibody of cotinine, is used to determine if the individual was a smoker from the fingerprint residue. The anti-cotinine nanoparticle conjugates were pipetted onto fingermarks and incubated after the addition of a fluorescent agent. Fingermarks from non-smokers were also developed but the lack of fluorescence indicated that cotinine was not present and the individual was not a smoker. Ag(20nm), Au(10&30nm), TiO₂ (15nm) can be utilized for the enhanced detection of illicit drugs from the fingerprint sample^[5,7,9,11].

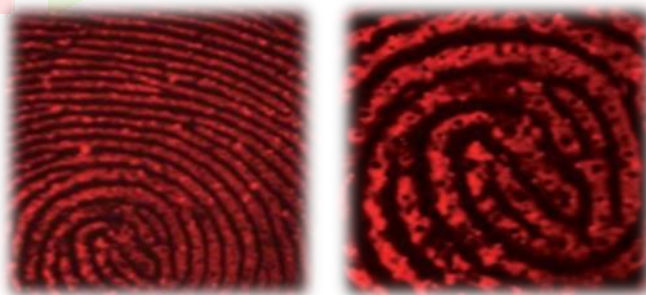


Fig 2:-Detection of cotinine in a fingerprint using anti-cotinine/gold nanoparticle conjugates and a secondary antibody fragment tagged with Alexa 546 dye. The fluorescence images shown in (a) and (b) are of the same fingerprint section but at two magnifications.^[7]

Nanosensors with melamine modified gold nanoparticles is used to identify drug clonazepam (date rape drug) from blood and skeletal remains. Citrate stabilized AuNPs are used as a probe and smartphone camera as an analysis device for rapid detection and quantification of codeine sulphate. Postmortem drug screening of lidocaine hydrochloride from vitreous humour by utilizing mobile application^[3,5,12]. Nafion modified Carbon paste electrode (CPE) can be used for the voltammetric determination of morphine. Methamphetamine can be recognized by using

SPR immunosensor. Nano chip based detection can be used for the detection of drugs such as gamma Hydroxybutyrate, Benzoylecgonine, and cocaine detection. Magnetically and optically actuated nanoparticles are used for multiplex drug detection^[10].

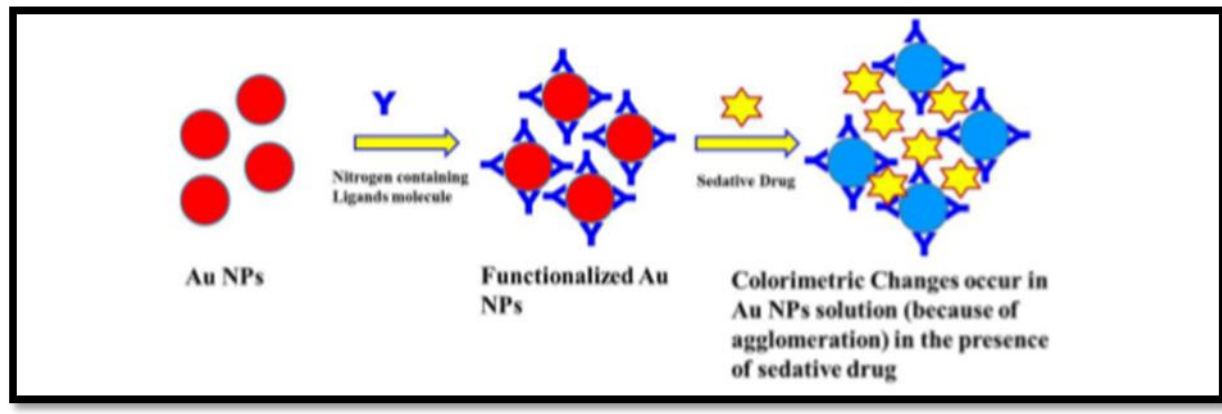


Fig 2.2:-Schematic diagram of gold nanoparticle interaction with clonazepam^[3]

3. Nanotechnology and Questioned documents

Nanoparticles are added on to the writing and printing ink, in its formulation. SEM images of the ink at various levels provides the elemental profile and morphological characterization of pigments present in writing and printing ink^[4]. Self-erasing medium and self-erasing ink have been made to help maintain security and secrecy of security documents. These are made of gold and silver nanoparticles of particles size 5nm each. These nanoparticles clump together and undergo color change when exposed to UV light. But in visible light, these clumps break and cause disappearing effect of the ink. Their self-erasing medium is an organic gel film, where the gold or silver nanoparticles are embedded in the gel film. Barcodes used in military security is made of highly secretive ink. Radio Frequency Identification Tags are made of ink containing gold nanoparticles encapsulated in an alkanethiol^[8].

The nanomaterials incorporated to the document can be analysed by Atomic Force Microscopy (AFM). It provides the qualitative information regarding the depth of the ink crossing, amplitude and phase changes of ink on paper, crossing sequence etc in a questioned document. It provides essential information for determining the sequence of lines made by ball pen ink and a ribbon dye^[1,11]. Luminescent nanoparticles such as quantum dots or nano sized luminescent phosphors and up converters can be incorporated as security tags to the security document to improve their security and thereby deter counterfeiting^[4,11].

4. Nanotechnology and DNA quantification

Lin and his colleagues first utilized gold nanoparticles of size (0.7nm of 13mAu) to enhance the PCR efficiency. AuNPs have superb heat transfer property and its property to enhance electro-chemiluminescence (ECL). It thereby decreases the reaction time while heating or cooling the thermal cycle and thereby the rate is increased. The utilization of these nanoparticles improves the sensitivity of the conventional approx. 5-10 times and more than 10,000 times in real time PCR.^[1,2,3,6,11]

Micro fluidic system can be utilized in post Polymerase Chain Reaction (PCR) quantification. The DNA samples can be quantified even in nanoliter range using commercially available Agilent 2100 bioanalyzer within 30 minutes. Mitochondrial DNA quantification can be conducted by using this system in many forensic science laboratories. Magnetic nanoparticles, silica based magnetic nanoparticles and copper nanoparticles for extraction of good quality PCR ready. Pan et al. apprehended hot start like effect in gold nanoparticle-based PCR, which has

promising applications in nanobiological and biomedical studies. DNA extracted from urine using organic reagents while carboxylated magnetic nanoparticles are used as solid phase adsorbents to isolate intact DNA for PCR amplification^[1,2,8,11].

5. Nanotechnology in Explosives detection

The ability of nanostructures to function as sensors of various chemical and biological compounds are considered for the detection of explosive substances. The detection of trace amounts of explosive is a challenging task because of number of issues, such as low quantity of unexploded explosives, contaminated samples, and different sample collection procedure. Electronic noses, nanocurcumin based probe, lasing Plasmon nanocavity, nanowire/nanotube and nanomechanical devices are nanosensor concepts are having strongest potential to form viable technological platforms for trace explosive detection. For ex: the polymer particles and nanoparticles that, when bound to an explosive molecule, change one of their measurable properties by providing high specificity detection of explosives. Recently, an antibody was developed against the explosive pentaerythritol tetranitrate (PETN)^[5,11]

Nanotagging can be utilized to detect the presence of GSR residues. High-resolution scanning electron microscope (SEM) imaging can be used to identify gunshot residue and in combination with X-ray spectrometry, helps to determine the elemental constituents of gunshot residue. Pandya et al. 2012 have revealed that turmeric extracted curcumin nanoparticles-based, highly selective, and ultrasensitive fluorescent probe can be used for the Trinitrotoluene (TNT) detection up to 1 nm level in aqueous solution. Chu et al. 2015 proposed a novel sensing technique for a label-free and selective detection of 2,4, 6-trinitrotoluene (TNT) from 10^{-12} to 10^{-4} M based on amine-terminated nanoparticles.^[3]

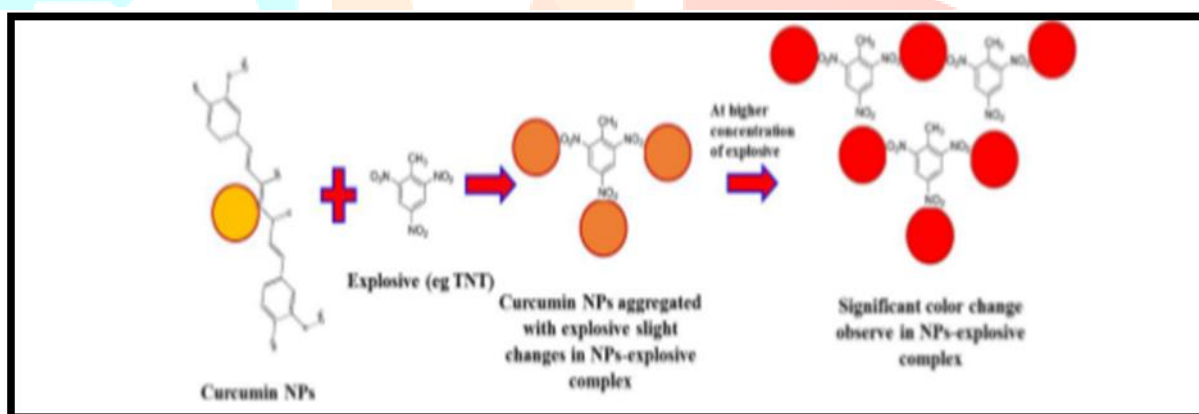


Fig 5: -Schematic representation of interaction between nano curcumin and TNT.^[3]

TABLE 1: Nanoparticles and its forensic applications

S.no	Nanoparticles	Broad Area	Use	Examples	References
1.	SiO ₂	Fingerprinting	Detection of latent fingerprinting	Optical properties incorporated to functionalized SiO ₂ particles detect latent finger prints	[7,13]
2.	Luminescent Quantum Dots CdS capped with ZnS and functionalised with Octadecanamine	Fingerprinting	Latent Fingerprint development	The fluorescence from the lipid fraction present in fingerprint residue, develops latent fingerprint.	[4]
3.	Colloidal gold with octadecanethiol, dissolved in petroleum ether	Fingerprinting	Latent Fingerprint development	Fingerprints developed on both porous and nonporous surfaces.	[4,8,7]
4.	AgNPs	Fingerprinting	Latent Fingerprint development	Fingerprint developed by Silver Physical Developer Method.	[4,5]
5.	AuNPs	Fingerprinting	Latent Fingerprint development	Latent fingerprint development by MMD SMD	[5,7,8,9]
6.	Au(10nm&30nm) Ag(20nm) TiO ₂ (15nm) NPs	Toxicology	Detection of drugs in fingerprint Residue using specific targets.	Au particles functionalized with anticotinine, detect the presence of cotinine by fluorescence.	[5,7,9]
7.	Cds	Fingerprinting	Development of Latent Fingerprint	CdS nanocrystal capped with dioctyl sulfosuccinate are applied on articles perfumed with cyanoacrylate and also on sticky ends of electrical tape without perfuming.	[1,3,9]
8.	CdSe/Zns	Fingerprint	Development of Latent Fingerprint	Fingerprints developed on non porous surfaces and fluoresce under UV	[2,5]
9.	Exfoliated Egyptian Blue NPs	Fingerprint	Latent Aged fingerprint Development	Fingerprints are detected with luminescence in NIR region	[15]
10.	ZnS capped with CdS nanocrystal	Fingerprinting	Latent Fingerprint Development	It reacts with the amino acids present in the FP residue.	[9]
11.	Au (0.7nm of 13nmAu)NPs	DNA	Enhancement of PCR efficiency	The PCR sensitivity gets enhanced for approx 10,000 times in real time PCR	[1,2,11]
12.	AuNPs and AgNPs (5mg each)	Questioned Document	Secret writing	Acts as self erasing ink and also as self erasing medium	[8]
13.	Au NPs	Security purpose	Radio Frequency Identification Tag	Ink containing Au nanoparticles encapsulated with alkanethiol marks tags or barcodes for military security purposes.	[8]

14.	Melamine modified AuNPs	Toxicology	Drug Identification	Acts as nanosensors which identify the drug Clonazepam(date rape drug) from blood and skeletal remains.	[3,5]
15.	Carboxylated Magnetic NPs, Silica based magnetic NPs and CuNPs	DNA	Quantification of PCR	Extraction of good quality PCR(DNA)	[5]
16.	Citrate stabilized AuNPs	Forensic Toxicology	Drug Identification	Detection and quantification of codeine sulphate by using smartphone application.	[3,5,10]

6. Nanotechnology based analytical applications

Nano-scale detection and analysis of materials can be performed using Transmission electron Microscope (TEM), Scanning Electron Microscope (SEM), Raman Micro-spectroscopy, Micro X ray Fluorescence (MXRF) technique and Atomic Force Microscopy (AFM). Among these techniques, AFM possess wide application range for forensic evidence analysis.

AFM micro-cantilever is used for selective detection. It can study the 3-D surface morphology and thereby provides the examination of ink crossings in document to determine the sequence of pen strokes. AFM is used for the quantitative assessment of the estimation of time since death, by analyzing the morphological changes of the blood cell. The deformation of cell and membrane surface of unfixed erythrocytes with time lapse is observed. Age of the blood spot can be determined from the dried bloodstain by analyzing the changes in the elasticity of erythrocytes in a nano-scale and thereby recorded using force-distance curve. The elasticity pattern decreases over time. AFM is used for the analysis of trace evidences such as textile fibres and pressure sensitive adhesives, by quantitatively measuring the surface texture parameters ^[1,3,11].

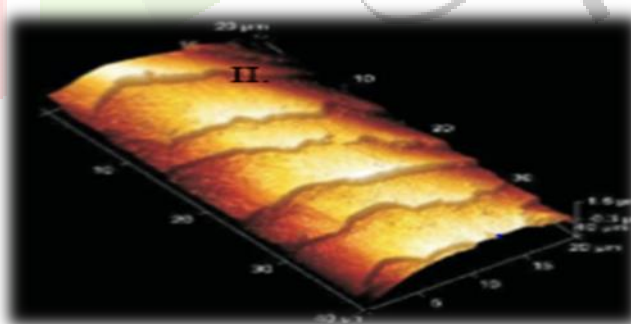


Fig 6.1:-The AFM image of Human eyebrow. The cuticle scale heights can be recorded statistically to differentiate hair origin (reproduced with permission of Mr. Yen-fou Chen, and Mr. Hungmin Lin of Taiwan Bruker).[1,12]

CONCLUSION

The transformation of bulky instruments into small chip-based system by nanoparticles shortens the analytical method to make investigations, sensitive, timely, and applicable. Nowadays nanotrackers and barcodes are used to combat the crime. The future may also embrace many possibilities for nanomaterial-based devices available for the detection and investigation of crime, surveillance, and tracking the missing or stolen items^[1,2]. Along with the positive aspects of nanotechnology application in forensic science, the negative aspects must also be considered. The translocation of nanoparticles in human organs due to chronic occupational exposure have toxicological impact^[1,2,8,14]. Biological materials such as DNA may get degraded and it may account for the release of nucleases from the putrefying cell, bacterial decomposition, cross linking, oxidation and deamination etc^[14]. In the near future, nanotechnology may assist as an innovative and preventive tool in the various field of forensic science like virtual autopsy, crime scene investigation, and more advancement in fields of fingerprint identification, questioned document, ballistics, and toxicology.

Conflict of Interest

None.

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