

■ ORIGINAL ARTICLE

Bio-polymeric Nano-particles for Prospective Forensic Applications: A Futuristic Approach

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ABSTRACT

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Despite its limited applications, nanotechnology has made significant contribution in a broad scientific arena. The technology is concerned with the development of new materials and reagents with conventional characteristics. Nano-particles are made from a variety of substances such as biopolymers, and synthetic polymers. The nano-particles synthesized from bio-polymers have benefits over synthetic polymeric nano-particles which include biocompatibility, non-toxicity, cost-efficiency and biodegradability. The use of nano-particles have gained a lot of attention in recent years. The use of the bio-polymeric nanoparticles provides new opportunities in surface-based applications. The fingerprint detection is based on surface phenomena to which nanotechnology can be applied. This article reviews the forensic application of bio-polymeric nano-particles and their use in development and enhancement of latent fingerprints. The use of nano-particles has emerged as a powerful tool for improved forensic analysis. It also provides deep insight into the future possibilities of nanotechnology.

KEYWORDS | nano-particles, bio-polymer, synthetic polymer, latent fingerprint

INTRODUCTION

Nano-science deals with the nanotechnology which involve the use of nano-materials. Nano-materials are very compressed length scale structures ranging from 1-100nm. Their significant size have advantages over microspheres (>1µm) due to their large surface area. Nano-particles can be easily manipulated based on their size and surface characteristics. Efficient methodologies can be developed with minimized pollutant effect by understanding the formation and growth of nano-particles. Nano-particles provide surface for the covalent linkage via

traditional coupling like carbodiimide-mediated amidation and esterification. Because of their efficient size, NPs are most preferably used in drug delivery system and can be easily absorbed by blood capillaries and cell barriers. Due to their multi-functional characteristics, NPs have varied range of applications in the field of agriculture, pharmaceutical, food packaging industries, medical sciences, and its blend with forensic techniques have improved effects in analysis tools.^{1,2} Nano-particles can be synthesized using different materials, like metals, semiconductors, synthetic



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polymers which possess adverse effects like toxicity risks and are non-biodegradable in nature. To overcome the side effects of these nano-particles, biopolymeric nano-particles can be synthesized from proteins and polysaccharides. These biopolymeric nano-particles revolutionized the world of bio-degradable, non-toxic and bio-compatible materials.^{3,4} In addition to various applications, nanotechnology has its significant use in Forensic science.⁷ Nanotechnology applications include pharmaceuticals, drug delivery systems and food packaging industries. Based on the characteristics like biosensing ability, nano-particle-protein linkage ability makes them suitable to be used as an aid to forensic analytical tools. The nano-particle-protein interactions can be used for multiple biological processes such as protein-protein interaction that can be used in fingerprinting analysis. The main goal of forensic analysis involve sensing of biological agents, diseases, and toxic materials. This paper gives an outline on the most available bio-polymers used for synthesis of nano-particles and their application in development and enhancement of latent fingerprints along with other future approach in forensic analysis.

Recently, there has been great interest in the use of nanotechnology in the design of new fingerprint detection systems. This is due to the fact that microparticles can provide improved latent fingerprint detection by using dye-functionalized microparticles (the dye or fluorophore may also be encapsulated within the microparticle) which can therefore provide an opportunity for improved visualization.

Bio-polymers used for preparation of nano-particles

Chitosan based nano-particles

Chitosan is the most abundant natural occurring biopolymer having excellent physiological and biological properties. Though it is not soluble in aqueous solution but graft modifications due to its functional groups it can be chemically modified to improve its solubility and as consequence increases its applications. It is a linear homopolymer constituted of β -(1,4)-linked N-acetylglucosamine units derived from crustaceans and insect exoskeleton. They are the major sources of chitin from which partially decacetylated polymer chitosan is obtained. It has excellent biological properties like non-toxicity, biodegradability,

mucoadhesive and antimicrobial properties which make it attractive even in biomedical field. Many of chitosan derivatives can also be obtained as it has active hydroxyl group and amino group that can undergo various chemical reactions such as hydroxylation, carboxylation, alkylation, acetylation, and esterification. These reactions help in acquiring the modified chitosan by introducing pendent group and destroying its crystal structure which consequently increases its solubility. These derivatives also increase its application except to be used in limited fields. Chitosan based nano-particles have the power to bind with the empty orbitals of some materials due to large number of lone pairs present in it. Mostly these are used in drug delivery, gene delivery, biosensors and in fractionated imaging. Chitosan nanoparticles can be prepared by ionic gelation method where the electrostatic interaction between the tripolyphosphate (TPP) and polyanion result in the formation of chitosan nanoparticles and hence the size of the chitosan nanoparticle can be controlled by controlling the concentration of chitosan and TPP under controlled pH conditions²⁴. Recently Chitosan based nanoparticles can be used for the enhancement of latent fingerprints due to its lipophilic nature. Chitosan aids in the attachment of nanoparticles to the frictional ridge and enhances contrast, making the fingerprint identification possible. The enhanced contrast evidently distinguishes the finger ridges and can be useful in the forensic identification.²⁵

Dextran Based Nanoparticles

Dextran is a linear polysaccharide of glucose that is derived from bacteria growing in sucrose-containing media consisting of 1,6-D-glucopyranosyl linkages. It is clinically approved and biologically safe polymer. NPs of dextran can be formed due to the presence of aldehyde group in dextran chain after the oxidation. The units of glucose in dextran can self-assemble to form nanoparticles by forming bonds with molecules like fatty acids and amines. They are suitable to form bio-conjugates and nanogels because of their inimitable physiochemical properties. Acetal-modified dextran nanoparticles contribute to class of biocompatible and degradable materials. These are specifically used in drug delivery system and treatment

therapies. Its low cost and availability is another reason that broadens its applications. It has good water solubility and non-toxic properties. Such physiological properties of dextran and its derivatives can add an aid to different analytical tools. The application of dextran-based nanoparticles in the field of forensic science is not much explored even dextran powders showed promising result in the enhancement of latent fingers on different surfaces. The smaller dextran particles adhere to the sweat and lipid present in the fingerprint residues and result in developing latent finger impressions.²⁶

METHOD & MATERIALS

Alginate-Based Nanoparticles Alginate is most of the widely investigated biopolymer in the area of nanoparticle preparation. It is naturally occurring anionic co-polymer of guluronic acid and mannuronic acid linked by a β-D-1-4 linkage, derived from cell of brown algae. It is a common pharmaceutical excipient and exhibit interesting biopharmaceutical properties, like pH sensitivity, low toxicity, biodegradability and biocompatibility. Alginate is a biodegradable, biocompatible polymer with very low toxicity. It has already claimed for the beneficial use due its properties in food and drug administration. Nanoparticulate systems made of biopolymers include promising properties as carriers and adjuvant for drug delivery as well use in the development of latent fingerprints. The nanoparticles of alginate can be

prepared easily by number of methods like spray drying, ionic gelation, emulsification etc. Recent Studies reported that alginate can be used for the lifting and enhancement of footwear in blood which suggest they can also be used for the lifting of latent fingerprints on different surfaces.²³

Protine Nanoparticles

Protein-based nanoparticles are very promising as their properties related to biodegradability, less immunogenic, and non-toxicity. Protein nanoparticles can be prepared from proteins like fibroins, albumin, gelatin, gliadine, legumin, lipoprotein, and ferritin. They are relatively easy to monitor in size and easy to prepare. Due their defined primary structures, the nanoparticles offers possibilities of surface modification. Albumin is found in blood plasma and has remarkable molecular properties to its functions and applications. The particles formed are usable aid to the medication and treatment. The particles were mainly employed for treatment and diagnosis of tumor. The particles can be modified as the vehicle for the drug carrier. Collagen the most abundant mammalian protein, the structural building material of vertebrates. It has a unique structure, size and amino acid sequences that forms triple helix fibre. Nanoparticles fabricated from collagen can be modified for wide applications which include improvement and addition of other proteins, such as elastin, fibronectin and glycosaminoglycans. Collagen based nanoparticles are thermally stable and readily sterilized. Gelatin is a natural water soluble macromolecule, acquired from dissolution and partial hydrolysis of collagen. It of two types obtained from different processes. Type A-gelatin is obtained by acid treatment of collagen and Type B-gelatin is obtained from alkaline hydrolysis of collagen. It has large number of functional groups which aid to the chemical crosslinking and synthesis of nanoparticles. Keratins are cysteine rich structures. These proteins exhibit a high mechanical strength owing to a large number of disulfide bonds. Keratins are most frequently used in formation of nanosuspensions. It can provide inexpensive alternative to collagen or fibronectin. It is also applicable in tissue engineering. Gelatin lifters are used in lifting the fingerprints enhanced

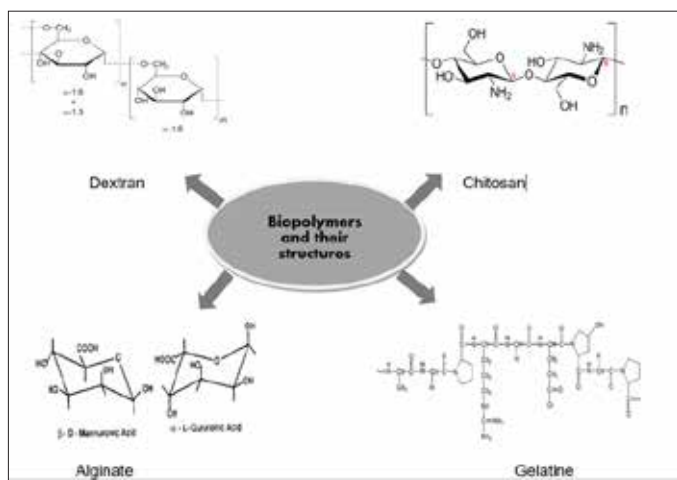


Figure 1 Biopolymers and their structures
Source: Author self.

using black powder. This is most effective method for lifting prints from the non-porous surface³⁶. Nanocellulosic hydrogels are used in detection of latent fingerprints and the latent prints developed by nanocellulosic hydrogels can be easily read under the UV light. Use of luminescent hydrogels assure detection and analysis of latent prints with good visual effects.

Use of Nanoparticles for Fingerprint Enhancement

The major organic component of a fingerprint residue consists of lipids. The biopolymeric nanoparticles consists of long carbon chains which render them lipophilic.

Due to protonation of the amine group of the cationic chain of the nanoparticles formed from biopolymers creates electrostatic force on attraction towards any other ligand like gold, this stabilises negatively charged glutamic ions adsorbed in nanoparticles. This forms colloids. When any biopolymer is capped to other material like silver and gold, it makes it lipophilic. When latent fingerprints are exposed to these colloids, lipids within residues are attracted to colloid formed and improves their contrast. Their applications in fingerprint development and visualization is broad due to their small size and higher surface area of reactivity. The reaction of functional groups present in biopolymeric nanoparticles binds with the amine group in fingerprint residues. The small size of these nanomaterials allows them to bind efficiently to the minute ridges and minutae present on the fingerprint. This efficient binding results in the superior imaging of the minute details along with sweat pores. Quantum dots and rare earth fluorescent like YVO₄, EU, and LaPo₄, Ce, Tb significantly created more attention due to their small size, excellent fluorescent intensity, good chemical and photostability. C-dots' possess photoluminescent properties and are highly responsive to analysis such as illicit drugs, explosives, pesticides, and heavy metals. The powders enriched with C-dots significantly provide strong background surface for the development of latent fingerprints providing collaborative approach between scientist and practitioners among broad spectrum of science.

Fabrication techniques

There are three frequently used fabrication methods for the preparation of nanoparticles using polysaccharides and proteins. Emulsification, desolvation and coacervation are the three most followed techniques. Emulsification is based on spontaneous mixing of organic and an aqueous phase. The organic phase is formed of homogenous solution of oil, lipophilic surfactant and water-miscible solvent while the aqueous phase consists of hydrophilic surfactant and water. This method is called the dissolution of hydrophobic substances in an organic solvent which is emulsified at very high shear.¹¹ This process results in formation of very small droplets (50-100nm). Solid nanoparticles, after emulsification by removing organic solvent through evaporation. Nanoparticles were also fabricated by using desolvation process where, desolvation factors such as natural salts or alcohol are added to protein solution. These desolvation factors changes the tertiary factors of protein. Due to crosslinking in reaching critical level with chemical substances it results in formation of nanoparticles. In two step desolvation, first step is to remove low molecule gelatin fractions present in supernatant by decanting and the second step is to redissolve the high molecule sedimented particle and desolvate again and again. Coacervation is similar to that of desolvation where the aqueous solution is mixed with solvent like acetone or ethanol to yield coacervates. Agents like glutaraldehyde are used to limit the coacervates. The basic difference between coacervation and desolvation is the factors like pH, Protein concentration, temperature end cross

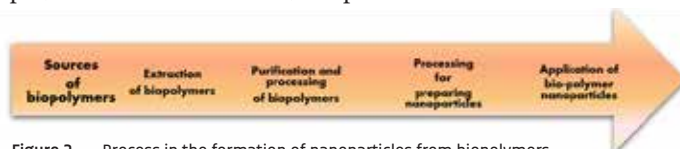


Figure 2 Process in the formation of nanoparticles from biopolymers. Source: Author self.

linkers, affecting the properties of the desired substance to prepare nanoparticles.

Application of biopolymeric nanoparticles in fingerprint analysis

The most common type of physical evidence is latent fingerprints. The visualization and enhancement techniques need to be modified with the advanced modus operandi. Criminals

using defined methods to secure themselves from being suspected. Fingerprints are known for its uniqueness and individuality and is therefore the most trusted method to identify a suspect. There have been different chemical and physical methods used for development of latent fingerprints, which involve Ninhydrin, iodine fuming, but some of them have toxic and destructive chemical properties that unintentionally can affect the identity of the original marks obtained. Moreover, the chemical used for the latent print development are non-biodegradable. These properties of some latent print developing agents generated a need for preparation of materials that can be used without a doubt of their ill effects. There are some studies that involve the use of materials which can be used as effective alternates to the present chemical materials. These materials are obtained from the natural sources in the form of natural polymers and known as bio-polymers. These polymers are more reliable due to their biocompatible nature, they are chemical less or non-toxic, they are biodegradable in nature and are cost effective. Their property of being easily modified they can be used for the fabrication of nanoparticles. These nanoparticles possess small and uniform size, good adhesion properties to the sweat residues. The sweat residues obtained on the different types of surfaces like non-porous, semi-porous and porous surfaces can be tested using these prepared nanoparticles for the presence of latent fingerprints. Chitosan based micropowders and conjugates were prepared using precipitating method and further ionotropic crosslinking using sodium tripolyphosphate as the crosslinking agent. The experiment was done to test the functionality and possibilities of realistic use of the prepared powder. The powder was tested on the oily fingerprint samples on the different surfaces glass (non-porous), rubber (semi-porous) and paper (porous) surfaces. The samples were left to reduce the residues for 24 hours, till development of prints using developed powders. The smooth structure of the glass resulted in acquiring a satisfactory result as compared to rubber and paper surfaces. The papillary lines were not clearly visible on rubber surface but provided a limited result. The results on paper surface was totally unsatisfactory due to the yellowish color of the paper surface selected for the experiment²².

Other experiment was performed to prepare four different dextran based powders using simple precipitation method and characterization was done to determine their potential application in latent fingerprint development. The initiating and crosslinking agents were used for obtaining aldehyde functionalities of the dextran chain and their crosslinking. This aimed for enhancement of fingerprints on interaction with residues. The small and uniform particles were allowed to bind with the fingerprint residues for their clear visualization²¹. These prepared formulation is less harmful and less costly. The results were not good on white paper. The dextran powders were easily handled and applicable. These bio-polymeric powders are non-destructive and irreversible loss of traces can be avoided.

Future Perspective

The researches are being conducted on the expanded applications of biopolymeric nanoparticles based on the properties that allow them to be used as an alternative to existing chemicals in latent print development. Due to their



Figure 3: Fingerprint identification using nanoparticles.

Source: Author self.

excellent promising factors, the bio-polymeric nanomaterials hold a wide range of forensic applications. The previously developed functional nanomaterials has also been widespread in this field⁹. The bio-polymeric nanomaterials can be developed for the use in bio-analytical techniques for analysis of biological evidences like DNA analysis due to its non-destructive properties. Their non-toxicity and cost effectiveness can lift them as the substitutes for the current chemicals used in forensic analysis. Nanomaterials can be used in developing biosensing tools that can be used in biosensors. The products can be used as taggants for the purpose of counterfeiting. The use of such naturally developed nanomaterials can assist to minimize the environmental hazards due to their eco-friendly nature.

RESULT AND DISCUSSION

This review discusses the advantages of using the nanoparticles from natural polymers. The most frequently used bio-polymeric nanoparticles including chitosan-based micropowders and dextran-based powders are described with their applications in development and enhancement of latent fingerprints on different surfaces. Being eco-friendly nature, these nanomaterials can be used as tool for minimizing hazardous effects of chemical materials used as forensic analytical

tools for ages. The smaller size of nanoparticles, good adhesion properties and higher surface reactivity makes it possible to develop latent prints and on reaction with silver and gold the electrostatic charge which makes it stable and helps in improvement in contrast of the developed prints. They support non-destructive and non-toxic behavior of the analytical methods used for sensitive forensic evidences and can be used as future toolkit in forensic applications. **IJFMP**

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