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Hybrid organic–inorganic silica based particles for latent fingermarks development: A review

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ABSTRACT

Recent progress in nanotechnology has led to the emergence of many new methods of latent fingermarks development. However, there is still need for a material that is easy to detect and has a high affinity to the latent fingermarks ridges. One way to combine these two features are hybrid organic–inorganic silica based composite materials. The chemical nature of silica lets for its simple modification with various organic moieties by organosilanes chemistry. Moreover, nanoparticles, quantum dots, molecules etc. can be easily embedded in the silicate matrix. In this work, the use of silica based materials for fingermarks development have been summarized. Three main groups of the materials have been isolated: SiO_2 based composites, porous phosphate heterostructures and desorption/ionization facilitating agents for surface-assisted laser desorption ionization time-of-flight mass spectrometry.

1. Introduction

Fingermarks are one of the most important group of physical evidence used for an individual identification in forensic science. Their usage for person identification is based on the fact that there was no individual ever found who has ridge patterns on the hands and feet identical with any other person [1]. This unique property of human ridge patterns makes fingermarks useful tool to link an exhibit with a certain person.

The Locard's Principle claims that it's impossible to act with the intensity related with a criminal action without leaving multiple traces [2]. The crime scene is usually full of traces. The biggest challenge is to find them and to understand their meaning. There are several types of fingermarks. Only few of them can be seen with a naked eye. The vast majority, are so called latent fingermarks that need to be developed before they can be seen, recorded and used in an investigation process. Up to now, there have been various methods proposed for latent fingermarks development. The most frequently used ones are: powder dusting, small particle reagent (SPR), cyanoacrylate and iodine fuming, methods based on ninhydrine and its analogs, physical developer (PD), vacuum metal deposition (VMD), multi metal deposition (MMD), single metal deposition (SMD) etc. [1]. The multiplicity of the methods is caused by the diversity of the latent fingermarks that can be found on a crime scene. The fingermarks can be deposited on porous or non-porous surface but also on adhesives, metals, fabric, human skin and many more. They can also be blood-based. Fingermarks can be also divided by the residue composition. Most of fingermarks are composed of eccrine and sebaceous fractions. Eccrine fraction is mostly composed with inorganic compounds, amino acids, proteins, lipids and miscellaneous compounds such as lactate, urea, creatine, creatinine, glucose and many others. The sebaceous part are fatty acids, phospholipids, wax esters, sterols, squalene and other organic compounds [1]. One should bear in mind that the composition of human sweat and sebum is an individual feature. Moreover, it changes with an individual's age, health condition, diet and so on. The fingermark already deposited on the surface also changes with time. The volatile components of the mark evaporates. The composition changes with light exposure, temperature and humidity [3]. In the case of porous surfaces, fingermark components diffuse with time into the material. Various components move with different velocity, what causes the changes in fingermark surface composition [4]. To manage the above mentioned diversity many different methods have been proposed to develop various types of latent fingermarks over the years. The classic, latent fingermarks development methods, have been already reviewed in several papers [5] and textbooks [1,6].

New, non-conventional methods for latent fingermarks development are still being introduced [7]. Among the others, various electrochemical methods have been proposed recently. There are several papers on latent fingermarks development by electrodeposition of conducting polymers such as polyaniline [8], poly(3,4-

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ethylenedioxythiophene) (PEDOT) [9], polypyrrole [10] and poly (pyrrole-co-EDOT) copolymer [11]. Other materials such as gold or silver nanoparticles [12], prussian blue [13], graphene [14] or copper [15] have been also electrodeposited in order to develop latent fingermarks. An interesting group of methods are those utilizing electrochemiluminescence (ECL) [16–18]. ECL have been successfully used to detect explosive residues [19]. Recently, a highly sensitive method for latent fingermark development have been designed by combining ECL with immunodetection [20]. Scanning electrochemical microscopy (SECM) have been used to visualize latent fingermarks pre-modified with metallic deposits [21,22]. Fingermarks developed with vacuum deposited Al-doped ZnO thin film has been also visualized with SECM [23]. Finally it was demonstrated that SECM is a suitable tool to develop latent fingermarks on conductive surfaces without previous modification [24].

An alternative approach is designing of a new, effective developing agents. In the late 80s a new group of such agents based on nanomaterials starts to grow. Nanoparticles based methods have been already summarized in several review papers [25–27]. Briefly, the first group of methods—multi metal deposition (MMD,) based on gold nanoparticles [28] was introduced in 1989 [29] and later modified [30,31]. The original method was further modified resulting in single metal deposition (SMD) [32] and one-step single metal nanoparticles deposition (SND) where glucose stabilized gold nanoparticles have been used [33]. Modification of gold nanoparticle surfaces with a ZnO layer enabled observation of fingermark luminescence [34]. Gold nanoparticles can be selectively bound to the fingermark [35] or to the porous surface [36,37]. The latter approach helps to overcome problems with variable fingermarks composition. The affinity of gold nanoparticles to the latent fingermark surface can be increased by their modification with antibodies [38]. Besides of gold, also nanostructures from different materials have been used. Standard physical developer (PD) can be used as an example of silver nanoparticles utilization for latent fingermark development [39]. CdS quantum dots modified with dendrimeric polymers [40] and CdSe/ZnS modified with octadecylamine [35] have been described. Chitosan stabilized CdS have been successfully used for latent fingermarks development on aluminum foil [41]. CdSe nanoparticles stabilized with mercaptoacetic acid have been used for latent fingermarks development on the sticky side of adhesive tape [42] while CdTe have been used for bloody fingermarks development on non-porous surfaces [43].

The diversity of fingermarks' types is a real challenge for the forensic science. Despite nanotechnology, which brought many new tools to forensic laboratories, there is still need for the new materials for latent fingermarks development. When searching for a new latent fingermark developer one should take into account two main features of the material. First of all, the material should be easy to detect. It may be colorful, fluorescent, phosphorescent etc. Secondly, it should have a diverse affinity to the fingermark ridges and to the material on which the fingermark have been deposited. It is a difficult task to find a single material that combines the two above mentioned features. The solution to this issue are hybrid, organic–inorganic composites. A suitable base for this type of materials are silica particles. The silicate matrix can be modified with, an easy-to-detect elements such as quantum dots, organic dyes etc. while their surface properties can be easily tuned with organosilanes chemistry. Hybrid silica-based particles of various sizes, structure and functional groups have been used in numerous applications [44], but only recently they have been tested as a novel latent fingermark developing agents. The aim of this review is to summarize the above mentioned efforts.

2. SiO_2 based composites

The first two papers on silica based composites for latent fingermarks development have appeared in 2008 [45,46]. Liu et al. [45] have entrapped Eu^{3+} sensitizer complex in sol–gel processed SiO_2 matrix. Authors have tested 1,10-phenantroline (OP) and thenoyltrifluoroacetone (TTFA) as sensitizers. The Eu^{3+}/sensitizer silica xerogels have been obtained by reacting sol–gel precursors such as tetraethoxysilane (TEOS), tetramethoxysilane (TMOS) and tetrakis (2-hydroxyethyl) orthosilicate (TKIS) in the presence of complex followed by drying procedure. The synthesis was found out to be time consuming. Xerogel fabrication process lasts for 28 days. In order to facilitate fingermarks dusting, resulting xerogels were grounded with mortar into a fine powder and mixed with magnetic powder. The best results have been obtained

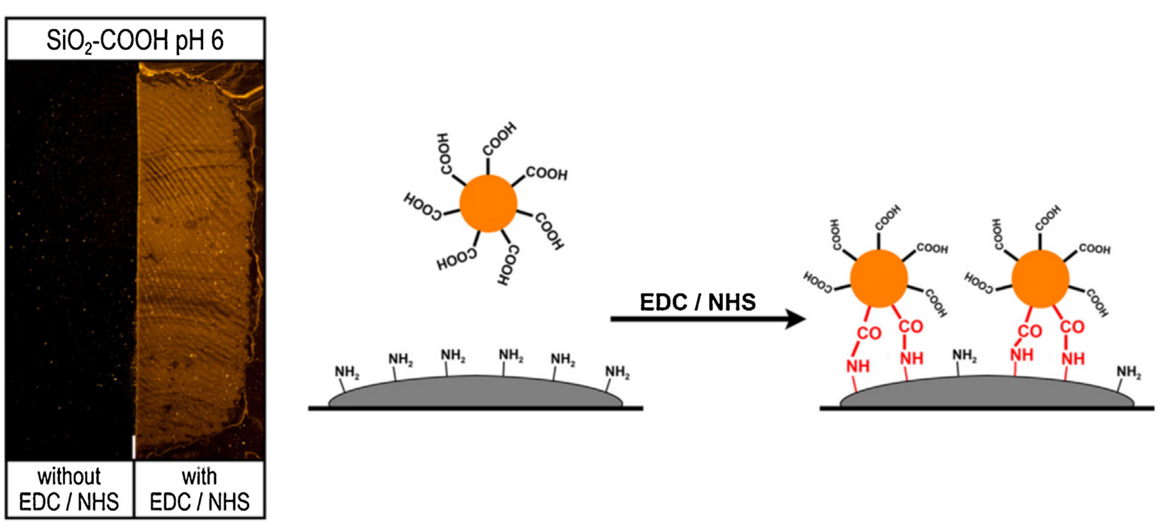

Fig. 1. Results obtained after application of SiO_2–COOH NPs at pH 6. For the right half, EDC/NHS is used to mediate the reaction. On the right is a schematic illustration of the bond formation between carboxyl groups present on SiO_2 NPs surface and amine groups found in the fingermark secretion. The amide linkage is mediated by the use of EDC/NHS [48].
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