Abstract

Fingermarks, as important evidence confirming the presence of a given person at the crime scene, are often invisible to the naked eye. Hence their visualisation requires particular development methods depending on the surface type on which the fingermark is deposited. A broad range of optical methods for latent fingermark visualisation has been developed over the years. These methods are based on the photoluminescence phenomenon, where the luminescent developing agent selectively interacts with fingermark residue and emits visible light upon the irradiation. However, these methods sometimes fail when latent fingermarks are deposited on porous, glossy, reflective, colourful, patterned or immensely luminescent surfaces. The goal of this thesis was to develop an effective optical method of detection fingermarks deposited on porous and non-porous, patterned, coloured surfaces or those exhibiting its own luminescence with the use of composite materials which have particular optical properties such as long-lived luminescence or upconversion, and which selectively interact with fingermark residue.

The first part of my thesis involves the study of the potential application of silica particles as a host for luminophores applied for fingermark visualisation. Silica particles have been surface-modified with a variety of organic moieties to enhance the affinity to the fingermark secretion. Several possible interactions between the fingermark components and surface-modified silica particles have been investigated, including thiol-gold interactions between gold nanoparticles deposited on the fingermark within the Single Metal Deposition technique (SMD) and thiol-modified silica particles, lipophilic interactions between sebaceous components of the fingermark (free fatty acids, triglycerides, waxes, squalenes etc.) and silica particles modified with lipophilic moieties like phenyl groups or long hydrocarbon chains, and amide bond formation between the amine groups present in fingermark secretions and carboxyl-modified silica nanoparticles. Since silica particles modified with lipophilic groups have shown the highest potential for fingermark development, these moieties were chosen for further research on the luminescent fingermark developer.

In the next part of the thesis, a detailed study of the properties and potential forensic applications of surface-modified silica particles with encapsulated luminophore is described. Two various luminescent developing materials, such as zinc oxide quantum dots encapsulated in a silica matrix and silica-coated upconverting crystals based on sodium yttrium fluoride doped with ytterbium and erbium ions, have been synthesised. Both these materials were surface-modified with lipophilic moieties to provide desirable selectivity to fingermark ridges. Due to the relatively long luminescence lifetime equal to 0.5 ms, zinc oxide quantum dots in the silica matrix have been investigated as a latent fingermark enhancement agent on reflective, colourful, adhesive or luminescent surfaces such as aluminium foil, magazine paper, sticky side of the tape, beverage cans, or copy paper. Utilising a time-gated imaging method for fingermark visualisation, it was possible to separate the fingermark luminescence from the background interference for most investigated substrates.

Silica-coated upconverting particles have been studied in terms of fingermark visualisation on reflective, patterned, or colourful surfaces. Due to the large anti-Stokes shift, the upconverting particles emit strong luminescence when irradiated with infrared light. Since in most natural surfaces or consumer products the upconversion is rare, the upconverting particles can be advantageous in fingermark detection on multicoloured surfaces, leading to background interference or autofluorescence elimination. The upconverting crystals were synthesised either in the hydrothermal

synthesis or solid-liquid-thermal-decomposition process and further coated with a silica layer and surface-modified with lipophilic moieties. Upconverting crystals were involved in the systematic evaluation of fingermarks deposited on several surfaces such as aluminium foil, glass, polymer foils. Fingermarks developed by modified upconverting particles have been compared to fingermarks enhanced by cyanoacrylate fuming followed by Rhodamine 6G staining to examine their potential to suppress background interference. Although the benchmark method of cyanoacrylate fuming with rhodamine staining performed better on most of the investigated fingermarks and surfaces, the upconverting particles may be a promising candidate for fingermark visualisation on highly luminescent or multicoloured surfaces like beverage cans where the conventional method is less efficient due to the background interference.

The last thesis part describes the study of the interactions between the europium complex and oleic acid, L-serine and squalene as the representative fingermark components. Fingermarks in this study were deposited on highly luminescent surfaces like copy or notebook paper. The complex of europium and thenoyltrifluoroacetone ($[Eu(TTA)_3(H_2O)_2]$) exhibits *in situ* changes in the luminescence properties when interacts with fingermark residue. Europium complex, distributed over the entire sample, reacts only with fingermark components generating locally new compounds with a longer luminescence lifetime than the initial complex. Thus, this phenomenon facilitates the fingermark enhancement by time-gated visualisation with no need for selective deposition of the developing agent on fingermarks and regardless of the background interferences because of the difference in the luminescence decay times of the complex on the fingermark and beyond is large enough. Commonly used amino acid reagents such as ninhydrin and 1,2-indanedione were applied for fingermark enhancement on paper substrates as the benchmark methods. It was found that the europium complex developed fingermarks with significantly better quality and higher contrast than ninhydrin and comparable quality and contrast than 1,2-indanedione. However, in samples exposed to water, only the europium complex enhanced the fingermark due to interactions with fingermark components that are hardly soluble or insoluble in water, unlike ninhydrin or 1,2-indanedione.

The results of the research and general conclusions were finally summarised. Furthermore, the possible future directions for optical imaging methods using luminescent sensitisers were also presented.

Date of preparation: 20.05.2021