Novel Fingermark Detection Techniques Using Upconverters with Anti-Stokes Luminescence

By

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Certificate of Authorship/Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

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Abbreviations

AA: Azelaic acid

AFIS: Automatic fingerprint identification system

AOT: Sodium bis(2-ethylhexyl) sulfosuccinate

CA: Cyanoacrylate

CAF: Cyanoacrylate Fuming

CTAB: cetyltrimethylammonium bromide

DNA: Deoxyribose Nucleic Acid

FTIR: Fourier transform infrared spectroscopy

IR: Infrared

NIR: Near infrared

PEI: Polyethylenimine

PVP: Polyvinylpyrrolidone

SEM: Scanning electron microscope

SLR camera: Single-Len Reflex camera

SPR: Small particle reagents

UC: Upconverter

UCNP: Upconverter nanoparticle

UC-AA: $NaYF_4$:Er,Yb/azelaic acid

UC (Ho)-AA: $NaYF_4$:Ho,Yb/azelaic acid

UC (Tm)-AA: $NaYF_4$:Tm,Yb/azelaic acid

UC-AOT: $NaYF_4$:Er,Yb /sodium bis(2-ethylhexyl) sulfosuccinate

UC-PEI: $NaYF_4$:Er,Yb/polyethylenimine

UC-PVP: $NaYF_4$:Er,Yb/polyvinyl pyrrolidone

UV: Ultraviolet

VSC: Video Spectral Comparator

XRD: X-ray diffraction

Publications and Manuscripts Arising From This Work

1. Rongliang Ma, Ronald Shimmon, Andrew McDonagh, Philip Maynard, Chris Lennard, and Claude Roux, Fingermark detection on non-porous and semi-porous surfaces using YVO_4:Er,Yb luminescent upconverting particles. Accepted， doi:10.1016/j.forsciint.2011.10.033.

2. Rongliang Ma, Elicia Bullock, Philip Maynard, Brian Reedy, Ronald Shimmon, Chris Lennard, Claude Roux, and Andrew McDonagh, Fingermark Detection on Non-Porous and Semi-Porous Surfaces Using NaYF4:Er,Yb Up-converter Particles, *Forensic Science International*, 207 (2011) 145-149 ， doi:10.1016/j.forsciint.2010.09.020.

3. Rongliang Ma, Andrew McDonagh, Chris Lennard, Ronald Shimmon, Philip Maynard, and Claude Roux, 'Latent Fingermark Detection Using Functionalised Upconvertors', presented for the BIT's 2nd Annual World Congress of Forensics, September, 2011, Chongqing.

4. Rongliang Ma, Ronald Shimmon, Andrew McDonagh, Philip Maynard, Chris Lennard, and Claude Roux, 'Further Research into Novel Fingermark Detection Techniques Using Upconversion Luminescence', presented for the 8th International Fingerprint Research Group (IFRG) Meeting, September, 2011, Helsinki.

5. Rongliang Ma, Ronald Shimmon, Andrew McDonagh, Philip Maynard, Chris Lennard, and Claude Roux, 'Fingermark Detection Using Anti-Stokes Luminescence Generated by Functionalized Up-onverters', paper presented on the 20th Symposium on the Forensic Sciences, Australian and New Zealand Forensic Science Society, 2010, Sydney.

6. Rongliang Ma, Ronald Shimmon, Philip Maynard, Chris Lennard, Andrew McDonagh, and Claude Roux, 'Further Research into Novel Fingermark Detection Techniques Using Anti-Stokes Luminescence', paper presented on the 5th European

Academy of Forensic Sciences, European Network of Forensic Science Institutes, 2009, Glasgow.

7. Rongliang Ma, Ronald Shimmon, Andrew McDonagh, Philip Maynard, Chris Lennard, and Claude Roux, 'Further Research into Novel Fingermark Detection Techniques Using Upconversion Luminescence', paper presented on the 7th International Fingerprint Research Group (IFRG) Meeting, June-July 2009, Lausanne.

Abstract

Fingerprinting is a mainstay of forensic science and has been used in crime investigation for more than one hundred years. However, most fingermarks found at a crime scene are latent; they may become visible through development and enhancement. Among all the fingermark development techniques, conventional luminescence methods are routinely employed, with the advantages of being both sensitive and selective on non-luminescent substrates (i.e., providing high contrast in developed marks).

Anti-Stokes luminescence or upconversion is an optical process of converting long-wavelength radiation into a shorter-wavelength emission, which is contrary to conventional Stokes luminescence. Upconversion mainly exits in rare-earth complexes and upconversion materials are referred to as upconverters. Commercially-available upconverters have been widely employed in security inks and biolabels.

Upconversion is unusual in both natural surfaces and in consumer products. If the upconverters are applied for fingermark detection and show selective affinity to fingermark materials, theoretically the strong luminescence of the upconverters can be visualised on fingermarks as bright regions on a totally dark background. This means that fingermark detection techniques using upconverters has the potential to eliminate interference from background printing and luminescence.

This thesis begins with the review of luminescence-based fingermark detection techniques and previous research on the application of upconverters for fingermark detection. The previous research showed that upconverters have an affinity for fingermark residues and are effective for fingermark detection.

Chapter 2 describes issues with respect to imaging the upconversion luminescence. Of the options tested, a 980 nm laser pointer with 700 mW output proved to be the most suitable light source for the excitation of the upconversion luminescence. Long exposure times were needed to record the upconversion

luminescence. A Rofin Poliview fitted with a 555 nm band-pass barrier filter was found to be a suitable recording system.

Chapter 3 investigates the application of the $NaYF_4$:Er,Yb upconverter powder for latent fingermark detection on non-porous and semi-porous surfaces. The $NaYF_4$:Er,Yb powder showed selective affinity to fingermark materials and the dry powdering method proved to be better than the suspension method. The upconverter powder showed strong luminescence when illuminated with 980 nm wavelength laser light and the developed fingermarks presented clear ridges with high contrast. A near-infrared laser diode and laser pointer are both effective light sources when used in conjunction with a 555 nm band-pass filter to block the IR light. In actual imaging, the fingermark substrate is still visible to some extent under long exposure times, but the interference is reduced compared to what is observed with conventional luminescence imaging and the fingermark detail is clear. In summary, the $NaYF_4$:Er,Yb powder can be used to detect fingermarks on various difficult surfaces that exhibit interfering background luminescence when using conventional luminescence techniques.

Chapter 4 investigates the application of another type of upconverter powder, YVO_4:Er,Yb, for fingermark detection on non-porous and semi-porous surfaces. The YVO_4:Er,Yb powder proved to be effective for latent fingermark development when used as a dry powder or as a suspension, with the former generally presenting the better result. The YVO_4:Er,Yb powder also showed selective affinity to fingermark residues on most surfaces and the developed fingermarks presented clear ridges against a clear background. The upconverter powder showed strong luminescence when illuminated with 980 nm wavelength laser light but was slightly less visually luminescent than the $NaYF_4$:Er,Yb powder. Both a laser diode and pointer are effective light sources when used in conjunction with a 555 nm band-pass filter to block the infrared light. As before, the fingermark substrate was visible to some extent in the upconversion luminescence mode with long exposure times, but the interference was reduced compared to that observed using conventional luminescence imaging. Clear fingermark detail was observed. In summary, the YVO_4:Er,Yb powder can be used to detect fingermarks on various difficult surfaces

that exhibit interfering background luminescence when using conventional luminescence techniques.

Cyanoacrylate fuming is probably the most important routine technique for fingermark detection on non-porous surfaces. In the fingermark detection process, the cyanoacrylate monomer forms a white fibrous layer of polycyanoacrylate on the fingermark ridges. There are numerous holes in the fibrous polycyanoacrylate layer, with an average diameter of 1–2 micrometres. Hence, it is worth investigating smaller $NaYF_4$:Er,Yb upconverter particles that can penetrate into the holes in the polymer structure and remain trapped inside. In Chapter 5, three methods (sieving, suspension and milling) were investigated to isolate the smaller particles from the commercial $NaYF_4$:Er,Yb powders. Owing to limitations with respect to instrumentation and time, no ideal results were acquired.

Conventional upconverter materials are insoluble in water and other solvents, and this limits their application when combined with cyanoacrylate fuming. The possibility of making upconverters soluble or dispersible in water was investigated by functionalizing them as nanoparticles with hydrophilic groups. Chapter 6 explores the synthesis and use of four functionalised upconverters including UC-PEI ($NaYF_4$:Er,Yb/polyethylenimine), UC-AA ($NaYF_4$:Er,Yb/azelaic acid), UC-PVP ($NaYF_4$:Er,Yb/polyvinyl pyrrolidone) and UC-AOT ($NaYF_4$:Er,Yb /sodium bis(2-ethylhexyl) sulfosuccinate) for staining CA-fumed fingermarks on various non-porous surfaces. Among them, the UC-PEI and UC-AA showed strong luminescence under 980 nm laser illumination, with the latter being more visually luminescent. The UC-PEI and UC-AA showed some advantages for fingermark detection on various difficult surfaces where background luminescence and printing interfered with conventional luminescence enhancement. Long exposure times under a Rofin Poliview system had to be employed in the imaging of fingermarks developed by the functionalised upconverters. These long exposure times resulted in the substrate itself being visible to some extent, which is different from the theoretical “ideal” scenario that would provide bright fingermarks against a totally dark background. However, functionalised upconverters still showed superior results to conventional

luminescence techniques for fingermark detection on some difficult substrates and they have great potential to be improved through further research.

General discussion and conclusions are presented in Chapter 7. Possible future directions for fingermark detection using upconverters are also presented.