1 Latent fingermark detection using functionalised silicon oxide nanoparticles:

2 Investigation into novel application procedures.

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6 Abstract

7

8 Investigations into the application of carboxyl-functionalised silicon oxide nanoparticles doped

9 with a ruthenium complex (RuBpy-doped CES-SiO$_2$ NPs) for latent fingermark development

10 on non-porous surfaces were reported in previous studies. These studies suggested that an

11 optimised NP-based method demonstrated advantages in fingermark selectivity and sensitivity.

12 To continue the series of research into using RuBpy-doped CES-SiO$_2$ NPs for fingermark

13 detection, the versatility and overall practicality of the optimised SiO$_2$ NP-based reagent for

14 latent fingermark detection and enhancement was evaluated.

15

16 When the optimised NP-based method was used in a repeated fashion (application of multiple

17 NP treatment cycles), it was found that the overall fingermark detection quality increased

18 across the evaluated fingermarks without a high risk of overdevelopment. The possibility of

19 incorporating the optimised NP-based reagent for potential operational use (e.g., at crime

20 scenes) was successfully demonstrated via spray application on three test surfaces (aluminium

21 foil, transparent polypropylene film and green polyethylene film). It was also shown that

22 further enhancement of "spray-detected" fingermarks was achievable via subsequent treatment

23 using the NP-based reagent in a colloidal dispersion bath. Additionally, the compatibility of

24 the optimised NP-based method with two-step cyanoacrylate fuming for latent fingermark

25 detection was evaluated. It was concluded that the two techniques are not compatible for

26 application in a fingermark detection sequence.

27

28 While encouraging results were demonstrated in this study, further optimisation and

29 comparison will be required before the multiple-treatment and spray-treatment approaches can

30 be considered for operational implementation.

Keywords

Fingerprints, impression evidence, multiple treatments, spray application, practicality, luminescence

1. **Introduction**

A simple definition of nanotechnology is the use of materials at the nanoscale [1]. Nanotechnology has been widely used in fields such as medicine (e.g., medical imaging and drug delivery) [2-5] and electronic applications (e.g., integrated optics) [6-8]. The application of nanotechnology for latent fingermark detection and enhancement is mainly achieved via the use of nanoparticles (NPs), which are particles with a diameter on a scale of nanometres (10^{-9} m). There are three advantages of choosing NPs for latent fingermark development: (i) their small particle sizes allow for high-resolution fingermark development [9,10]; (ii) modifiable surface structures enable fingermark detection with high selectivity [9,11]; and (iii) optical properties of NPs can be altered to produce luminescent fingermarks to minimise substrate background interferences [11-15].

The desirable features can be used to improve current limitations with latent fingermark detection including selectivity and sensitivity [16-19]. A significant number of different NPs have been reported in the literature for latent fingermark development. However, as reviewed by Kanodarwala et al. [20], most of the previously studied NPs have not fully utilised these potential advantages simultaneously. Multimetal deposition (MMD)-type techniques were proposed with a focus mainly on the size advantage offered by gold NPs [21,22]. A major drawback is that MMD-type techniques are not capable to produce luminescent fingermarks and developed fingermarks are low in contrast (e.g., grey fingermark ridges against a light grey background on white paper) [23-26]. While quantum dots (QDs) and carbon dots (C-dots) are both highly luminescent NPs, the majority that have been tested to-date do not outperform commonly used techniques such as cyanoacrylate fuming (CAF) and fingerprint powders [27-31]. Besides, no well-demonstrated advantages were shown using surface-functionalised QDs and C-dots for improved selectivity and sensitivity [32,33]. Upconverting nanoparticles (UCNPs) possess a rare optical property—anti-Stokes luminescence—that has shown potential

63   to produce improved fingermark contrast on highly luminescent substrates. However, there is

64   still a lack of optimisation and validation for the use of UCNPs for latent fingermark detection

65   and enhancement [34-39]. Furthermore, there are more limitations of using UCNPs for

66   fingermark detection. For example, high-quality UCNPs are difficult to synthesise and they

67   have a low commercial availability [40]. UCNP-developed fingermarks also require highly-

68   specialised and powerful source of illumination for imaging [34,35]. In addition, most of these

69   NP-based methods, including QDs, C-dots and UCNPs, have not focused on selective

70   interactions between the NPs and fingermark residues. As such, research is still required to

71   fully exploit the advantages possessed by NPs for latent fingermark detection.

72

73   Silicon oxide nanoparticles (SiO_2 NPs) are a type of NPs that are capable of providing a

74   combination of the three aforementioned favourable NP characteristics for latent fingermark

75   development [11,14,15,20]. Various studies have been conducted to investigate the use of

76   functionalised SiO_2 NPs for fingermark detection over the years. Although most of the research

77   has attempted to exploit the favourable features offered by SiO_2 NPs, none of the studies

78   demonstrated the use of the combination of the three desirable characteristics provided by SiO_2

79   NPs for improved selectivity and sensitivity. Most of the reported SiO_2 NPs were applied as a

80   dry powder [12,13,41-44]. This application route offered no clear benefits when compared to

81   conventional fingerprint powders and did not benefit from NP surface functionalisation to

82   target fingermark residues via chemical interaction. In addition, no in-depth fingermark

83   comparisons against routine detection methods were conducted in the aforementioned research

84   [45,46].

85

86   A study undertaken by Moret et al. in 2016, demonstrated the use of carboxyl-functionalised

87   SiO_2 NPs doped with a ruthenium complex (RuBpy-doped CES-SiO_2 NPs) for latent

88   fingermark detection, indicating a promising starting point for further research [11]. As a result

89   of this study, Lee et al. presented further research using the SiO_2 NP-based reagent for latent

90   fingermark detection and enhancement on non-porous substrates. First, various detection

91   parameters—NP concentration used in the colloidal dispersion, bath temperature and

92   immersion time—were modified and optimised [14]. Consequently, a refined RuBpy-doped

93   CES-SiO_2 NP-based method was then proposed. A reduction in the amount of CES surface

94   functionalisation was determined to provide improved fingermark detection effectiveness and

95   a shaking incubator was incorporated into the treatment process to offer a more practical

96   treatment approach [15]. While the overall fingermark detection effectiveness of the NP-based

97 method was judged to be inferior when compared to CAF with rhodamine 6G luminescent
98 staining (CAF-R6G), the absolute performance of the RuBpy-doped CES-SiO$_2$ NP-based
99 method was highly encouraging as a stand-alone fingermark detection technique. Moreover,
100 the optimised NP-based method demonstrated advantages such as high selectivity
101 (development of more homogeneous fingermark ridges with finer detail compared to CAF-
102 R6G development) and high sensitivity (ability to generate visible fingermark across different
103 weak fingermark donors) [15]. Therefore, further investigation was required to exploit the
104 notable benefits of using the optimised NP-based method for latent fingermark detection.
105
106 As a continuation of these two studies, the overall practicality of the optimised RuBpy-doped
107 CES-SiO$_2$ NP-based method was further investigated. According to the research guidelines
108 published by the International Fingerprint Research Group (IFRG), research into fingermark
109 detection techniques can be categorised into four phases (Phases 1 to 4) [47]. Together, these
110 four research phases provide a solid and fundamental framework for progressing new
111 fingermark detection techniques from pilot studies to potential operational applications.
112 Although fingerprint research conducted across these four research phases is commonly
113 reported in the literature [12,48-52], practical application by end-users including law
114 enforcement agencies and forensic laboratories tends to be overlooked. For example, complex
115 and labour-intensive reagent preparations have been suggested for self-synthesised fingerprint
116 powders that offer no apparent advantages over the use of conventional fingerprint powders
117 [53]. The first generations of MMD-type techniques also suffered from time-consuming
118 treatment procedures [21-24]. As such, the practical implementation and applicability of new
119 fingermark detection methods should ideally be considered during the early research stages.
120 Moreover, as suggested in the IFRG guidelines, it is also critical to evaluate the compatibility
121 of new detection methods with benchmark fingermark detection techniques when used in a
122 fingermark detection sequence [47].
123
124 This study investigated the versatility of the aforementioned optimised RuBpy-doped CES-
125 SiO$_2$ NPs as a reagent for latent fingermark development [14,15]. Novel application procedures
126 including multiple treatments using the NP-based method in a laboratory setting and a spray
127 method for potential onsite application to fixed surfaces by end-users were proposed.
128 Additionally, the compatibility of the SiO$_2$ NP-based method when applied in sequence with
129 CAF-R6G was evaluated.

2. <u>Materials and methods</u>

The experiments conducted in this study were performed as proof-of-concept work. Novel application procedures using the optimised RuBpy-doped CES-SiO$_2$ NP-based reagent for latent fingermark detection were evaluated. As such and in accordance with the IFRG research guidelines, this study was undertaken as a Phase 1 evaluation (pilot study) [47]. The experimental parameters (e.g., number of fingermark donors, types of substrates and collection process of fingermark specimens) were chosen to obtain a realistic assessment of each method's performance. The optimised RuBpy-doped CES-SiO$_2$ NP-based reagent was synthesised and applied following the synthesis and treatment procedures reported in the previous study [15]. The versatility of the optimised NP-based reagent was assessed via repeated treatments, spray application and application in sequence with CAF-R6G on natural fingermarks collected from three donors on three test substrates.

2.1   Materials

2.1.1 Chemicals

Ammonium hydroxide (NH$_4$OH) (30%), 1-hexanol, tetraethyl orthosilicate (TEOS), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (RuBpy), rhodamine 6G (R6G), Triton X-100 (TX-100), sodium chloride (NaCl) ($\geq$98%), isopropanol (reagent grade) and methyl ethyl ketone (reagent grade) were purchased from Sigma-Aldrich (Australia) and used as received. Cyclohexane (AR grade) and acetone (AR grade) were purchased from Chem-Supply (Australia) and used as received. Carboxyethylsilanetriol di-sodium salt, 25% in water (CES) was supplied by Novachem (Australia) and used as received. Type 1 ultrapure water (resistivity: 18.2 MΩ cm) used throughout the study was produced using an Arium® Pro Ultrapure Water System (Sartorius AG, Germany).

2.1.2 Instrumentation

An Eppendorf Centrifuge 5810 R (Eppendorf South Pacific Pty. Ltd., Australia) was used for centrifugation of the RuBpy-doped SiO$_2$ NPs during synthesis. A Zeiss Supra 55VP high resolution Field Emission Scanning Electron Microscope (FESEM) (Carl Zeiss Microscopy

163   GmbH, Germany) with a Schottky source was used for scanning electron microscopy (SEM)
164   on the RuBpy-doped CES-SiO$_2$ NPs. A Leica EM ACE600 high vacuum coater (Leica
165   Microsystems GmbH, Germany) was used to coat a layer of carbon film on the RuBpy-doped
166   CES-SiO$_2$ NPs prior to SEM analysis. A Malvern Zetasizer Nano ZS (Malvern Panalytical Ltd,
167   United Kingdom) was also used to determine the hydrodynamic diameter of the CES-SiO$_2$ NPs
168   in solution. A MVC$^®$ 1000 fuming cabinet (Foster + Freeman Ltd., United Kingdom) was used
169   with Cyanobloom (Foster + Freeman Ltd., United Kingdom) as the cyanoacrylate monomer
170   for cyanoacrylate fuming. A JSSI-100T Compact Shaking Incubator (JS Research Inc.,
171   Republic of Korea) was used to facilitate the fingermark treatment process. A Cole-Palmer
172   Trigger Spray Bottle (240 mL) and a Cole-Palmer Economical Glove Box (John Morris
173   Scientific Pty Ltd, Australia) were used to facilitate the spraying process for the RuBpy-doped
174   CES-SiO$_2$ NPs. A Rofin Polilight$^®$ PL500 forensic light source coupled with a Rofin
175   Poliview$^®$ imaging system (Rofin Australia Pty Ltd, Australia) were used for the visualisation
176   of treated fingermarks and for image processing.
177
178   **2.2   Methods**
179
180   *2.2.1 Synthesis and characterisation*
181
182   The RuBpy-doped CES-functionalised SiO$_2$ NPs were synthesised following the reverse
183   microemulsion procedure presented in the previous studies with the optimal CES amount
184   (50 µL) used for surface functionalisation [14,15]. Following the start of the synthetic
185   procedure and the first 24 hours of constant magnetic stirring at room temperature, 100 µL of
186   TEOS and 50 µL of CES were added to the reaction mixture for surface functionalisation. The
187   mixture was stirred for an additional 24 hours at room temperature before being centrifuged
188   and isolated. Finally, 0.6 g of the RuBpy-doped CES-SiO$_2$ NPs were collected and redispersed
189   in 20 mL of Type 1 ultrapure water.
190
191   To characterise the synthesised RuBpy-doped CES-SiO$_2$ NPs, SEM analysis and dynamic light
192   scattering (DLS) measurements were utilised. The same procedural details for SEM analysis
193   and DLS measurements presented in the previous study were followed [14].

2.2.2 Fingermark specimens

Three individuals—representing weak, average and strong fingermark donors—provided fingermarks in this study (fingermark donorship was determined based on previous experience developing latent fingermarks from these individuals). While the experiments undertaken in this study were conducted as proof-of-concept work, only natural (ungroomed) fingermarks were used to better mimic typical casework scenarios [47]. Prior to depositing fingermarks on substrates, donors were instructed to rub their hands together to achieve a homogeneous distribution of fingermark secretions across the fingertips. Donors were also asked to avoid handwashing 30 min before fingermark deposition but to otherwise undertake normal activities. Three substrates were used that represent commodity item surfaces; these were aluminium foil, transparent polypropylene (PP) plastic film, and green polyethylene (PE) plastic film [14,15]. Table 1 summarises the three test substrates used throughout the experiments.

Table 1: Summary of the three substrates used in this study [14,15].

Substrate	Description (Brand)
Aluminium foil	Caterer's aluminium foil (Alfresco, Australia)
Transparent PP film	A4 sheet protectors (Marbig, Australia)
Green PE film	Garden bags (Woolworths, Australia)

The fingermark specimens collected from the three donors on the three substrates were aged from three weeks to 13 months prior to treatment; 18 to 27 full fingermark specimens were used in each of the experiments. Split fingermark specimens were employed to compare different treatments, while the numbers of the left- and right-half deposits per treatment in any comparison were kept the same to reduce the impact of intra-donor variability across the depositions. All fingermarks were collected in four depletions. For each comparison experiment, fingermark specimens were used from the same depletion of each donor on each substrate. All fingermark specimens were stored in laboratory drawers under normal office conditions, with a mean temperature of $19.5 \pm 2.1°C$ and a mean relative humidity of $53.2 \pm 3.1\%$.

220 *2.2.3 Multiple treatments using the optimised nanoparticle-based method*
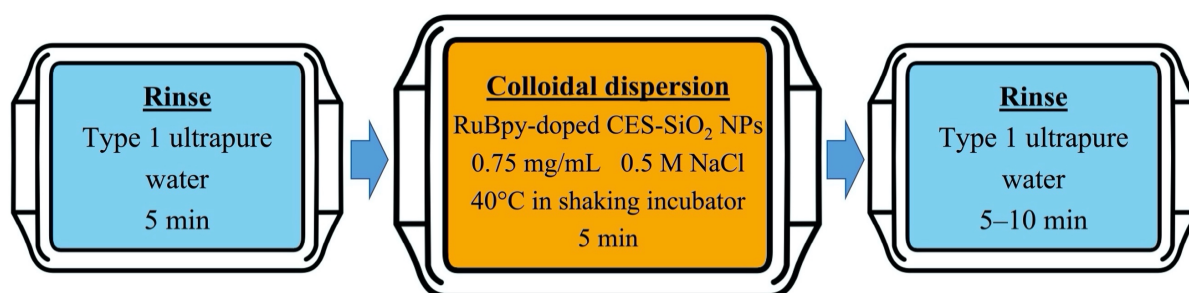
221

222 The impact on fingermark detection quality from multiple treatments using the RuBpy-doped

223 CES-SiO$_2$ NP-based method (i.e., multiple sequential treatments on fingermarks using the NPs)

224 was examined during this study. The optimised NP-based method was used (following the

225 procedure in the previous study [15]) in sequence on both split and full fingermark specimens.

226 In order to achieve this, the following protocol was applied:

227 1. Fingermarks underwent treatment using the optimised RuBpy-doped CES-SiO$_2$ NP-
228 based method (Figure 1).

229 2. Fingermarks were then left to dry on a laboratory bench before visualisation under the
230 optimal imaging conditions (Section 2.2.6).

231 3. Using a new, freshly-prepared colloidal dispersion, the same fingermarks underwent a
232 new treatment cycle using the NP-based method.

233 4. Steps 2 and 3 were repeated multiple times based on the experiments conducted.

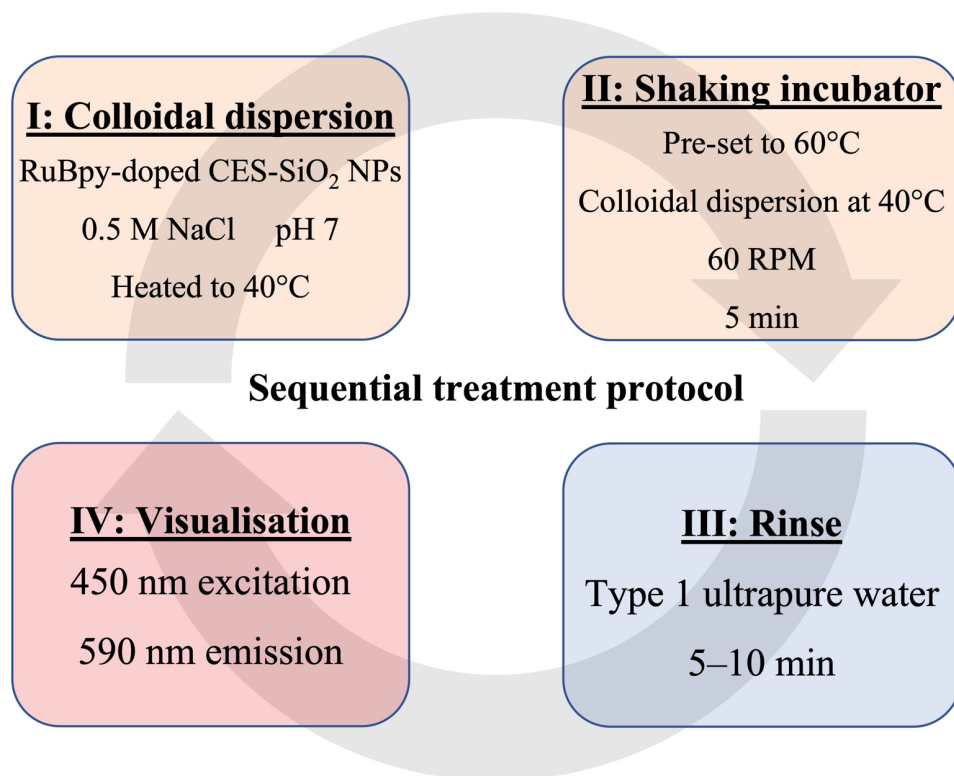234 5. The treated fingermarks were visualised in the luminescence mode (Section 2.2.6).

235

236 Note that fingermarks were rinsed with Type 1 ultrapure water prior to immersion into the

237 colloidal dispersion for the first treatment. For the sequential treatments (i.e., all consecutive

238 treatments after the first treatment), fingermarks were immersed into the colloidal dispersion

239 without being rinsed in a bath of Type 1 ultrapure water. Figure 2 is a schematic diagram

240 depicting the protocol for the sequential treatments using the optimised SiO$_2$ NP-based method.

241

Rinse
Type 1 ultrapure
water
5 min

Colloidal dispersion
RuBpy-doped CES-SiO$_2$ NPs
0.75 mg/mL   0.5 M NaCl
40°C in shaking incubator
5 min

Rinse
Type 1 ultrapure
water
5–10 min

242

243 *Figure 1: Schematic diagram illustrating the application procedure using the optimised*

244 *RuBpy-doped CES-SiO$_2$ NP-based reagent for latent fingermark development.*

I: Colloidal dispersion

RuBpy-doped CES-SiO$_2$ NPs

0.5 M NaCl   pH 7

Heated to 40°C

II: Shaking incubator

Pre-set to 60°C

Colloidal dispersion at 40°C

60 RPM

5 min

Sequential treatment protocol

IV: Visualisation

450 nm excitation

590 nm emission

III: Rinse

Type 1 ultrapure water

5–10 min

Figure 2: Schematic diagram depicting the protocol used in the study for the sequential treatments of fingermarks using the RuBpy-doped CES-SiO$_2$ NP-based method.

2.2.4 Spray application of the nanoparticle-based reagent

In this part of the study, the RuBpy-doped CES-SiO$_2$ NPs were applied as a spray to detect latent fingermarks on the three test substrates. Experiments were undertaken within a glove box (Cole-Palmer Economical Glove Box) to eliminate any potential inhalation of airborne NP droplets during the spraying process.

Various durations of application time (1 min, 2 min and 3 min) were examined in order to determine the optimal conditions. As part of the study, the fingermark detection effectiveness of the solution applied as a spray was compared with that of treatment by immersion. The protocol detailed below was followed for spray application:

1. 100 mL of the RuBpy-doped CES-SiO$_2$ NP colloidal dispersion was prepared and heated to 40°C using a hot plate. The colloidal dispersion was then transferred to a Cole-Palmer Trigger Spray Bottle that had been covered in aluminium foil to slow the cooling of the colloidal dispersion during the application process.

2. With approximately 30 cm between the nozzle of the trigger spray bottle and the fingermark specimens, a "mist" of the NP colloidal dispersion was sprayed onto the fingermark specimens for various durations of time (1 min/2 min/3 min) across a 50 × 30 cm area. 25 to 30 spray pumps (trigger pulls) were applied across the area per min. Each spray pump consumed approximately 0.9 mL of the NP colloidal dispersion.

3. The fingermarks were left to "develop" for 1 min.

4. The fingermark specimens were then rinsed for 1 min to remove background NP droplets by praying Type 1 ultrapure water from a clean Cole-Palmer Trigger Spray Bottle.

5. The fingermark specimens were rinsed in a bath of Type 1 ultrapure water for 5 to 10 min, then left to dry prior to visualisation in the luminescence mode (Section 2.2.6).

2.2.5 *Compatibility of the optimised nanoparticle-based method with CAF-R6G*

The compatibility of the optimised RuBpy-doped CES-SiO$_2$ NP-based method with CAF followed by rhodamine 6G staining (referred to as CAF-R6G or two-step CAF) was evaluated. Split fingermarks were used for evaluation of detection quality when the NP-based method was applied in sequence with CAF-R6G. Fingermark specimens were processed using the following protocol:

1. On a split fingermark specimen, the optimised RuBpy-doped CES-SiO$_2$ NP-based method and CAF-R6G were applied to treat the two respective split halves of the fingermark following the procedural steps documented in the previous study [15].

2. Both fingermark halves were left to dry naturally on a laboratory bench prior to visualisation under the respective optimal imaging conditions for each technique in the luminescence mode using a Rofin Poliview® imaging system (Section 2.2.6).

3. A new colloidal dispersion was used to treat the half fingermark that had been treated using CAF-R6G, while the NP-treated half fingermark underwent CAF-R6G treatment.

4. The two respective split halves were imaged under the respective optimal imaging condition for each technique in the luminescence mode (Section 2.2.6).

2.2.6 Fingermark visualisation and assessment

All processed fingermark specimens underwent a visual screening procedure first in a room with low light intensity (light settings that were similar to a darkroom for photography processing) to mimic operational procedures for processing fingermark evidence. Specimens with positive development observed during the screening procedure (i.e., detectable fingermarks under the conditions indicated below) were recorded using a Rofin Poliview® imaging system.

The fingermarks treated with the RuBpy-doped CES-SiO$_2$ NPs (by immersion and as a spray) were recorded in the luminescence mode with excitation at 450 nm. For the fingermark specimens processed with CAF followed by R6G staining, excitation at 530 nm was utilised. All fingermark images were captured with observation at 590 nm (using a 610 nm bandpass interference filter tilted by 30°) and saved in Tagged Image File (TIF) format. All fingermark images were captured in greyscale using the Rofin Poliview® system and no colour conversion was performed.

A lens aperture of f/8 was used for all images, and each test substrate was imaged with a constant exposure time for each of the two techniques. Fingermark halves in the comparison study between the RuBpy-doped CES-SiO$_2$ NPs and CAF-R6G were imaged with their respective optimal excitation, with corresponding fingermark halves then digitally stitched together using Adobe Photoshop® software. No digital enhancements were performed on any fingermark images captured during this study. Qualitative assessments of representative direct fingermark comparisons were accomplished using three assessors with experience in fingerprint research (no fingermark assessment scale was used). Fingermark assessment and evaluation for all the presented experiments were performed from a computer screen.

3. <u>Results and discussion</u>

3.1 Characterisation of the functionalised silicon oxide nanoparticles

Figure 3 is an SEM image of the RuBpy-doped CES-SiO$_2$ NPs and the corresponding size distribution analysis as measured by DLS, with an average diameter of 70.7 nm indicated. The average shape and size of the NPs were also uniform as observed from the SEM analysis. The DLS analysis indicated that the RuBpy-doped CES-SiO$_2$ NPs had a relatively narrow size distribution. From these results, the synthesised RuBpy-doped CES-SiO$_2$ NPs used in this study were determined to be similar to the NPs employed for the work described in the previous study (average diameter of 72.9 nm) [15]. This demonstrated that the synthesis procedure used to produce the RuBpy-doped CES-SiO$_2$ NPs optimised for latent fingermark development is robust and reproducible.
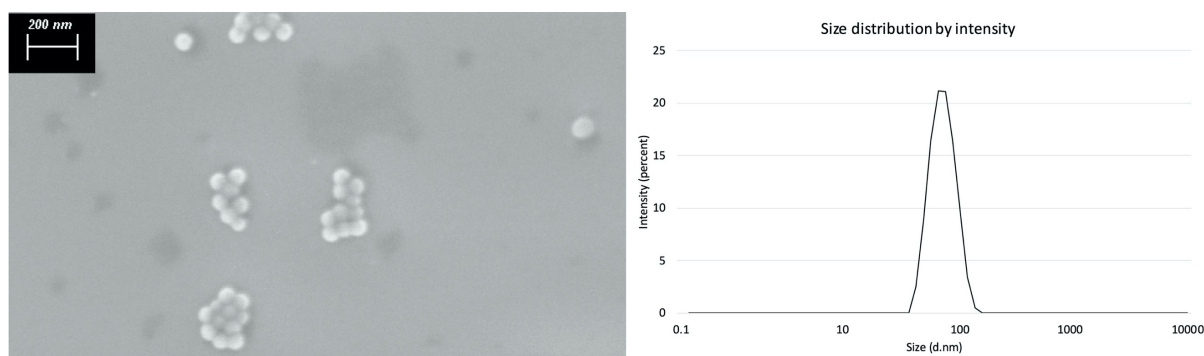
Figure 3: Example SEM image (left) and the size distribution analysis (right) of the RuBpy-doped CES-SiO$_2$ NPs synthesised for the experiments in this study. The average diameter of the SiO$_2$ NPs was 70.7 nm as measured by DLS. A relatively narrow size distribution of the NPs was also indicated.

3.2 Multiple treatments using the optimised nanoparticle-based method

In the previously-published comparison study between the optimised RuBpy-doped CES-SiO$_2$ NP-based method and CAF-R6G, the fingermark detection effectiveness of the NP-based method was judged to be inferior on the evaluated fingermarks. However, the optimised NP-based method demonstrated relatively good absolute fingermark detection performance, as well as lower donor dependency compared to CAF-R6G across the fingermarks evaluated [15].

346 Since the use of the RuBpy-doped CES-SiO$_2$ NPs demonstrated promising fingermark
347 selectivity and sensitivity, the effect of repeated application of the optimised RuBpy-doped
348 CES-SiO$_2$ NP-based method on fingermark detection quality was investigated.
349

350 *3.2.1 Comparison of multiple treatments with single treatment*
351

352 The feasibility of using the RuBpy-doped CES-SiO$_2$ NP based-method multiple times for
353 fingermark detection and enhancement was investigated through comparison to single
354 treatment (Figure 4). On the collected fingermarks across the three substrates, left halves of
355 fingermarks were treated with the NP-based method once while the right fingermark halves
356 underwent treatment for a total of three times (i.e., two more subsequent treatments using the
357 NP-based method). A freshly-prepared colloidal dispersion was used for each treatment.
358

359 It was observed that the overall fingermark detection quality was improved using multiple
360 treatments of the optimised RuBpy-doped CES-SiO$_2$ NP-based method. Across the illustrated
361 fingermarks (Figure 4), a slight increase in ridge clarity resulted from the second fingermark
362 treatment. A significant increase in ridge clarity and ridge detail resulted from the third
363 treatment using the NP-based method. For the fingermarks on transparent PP and green PE
364 films, improvements in enhancement quality were more pronounced between the second and
365 third treatments than that of the first and second treatments. Note that the fingermarks on
366 aluminium foil were treated with the NP-based method two times instead of three, as relatively
367 heavy background staining was observed after the second treatment.
368

369 With the evaluated fingermarks it was noted that, after the third fingermark treatment, the
370 difference regarding the overall detection quality was not substantial between the two stronger
371 donors (donors 1 and 2) and the weak donor (donor 3). For instance, on the transparent PP and
372 green PE films, the respective enhancement of the fingermarks across the three donors after
373 the third treatment was consistently good. Although this was a proof-of-concept experiment,
374 with a limited number of fingermark specimens and substrates, the application of the NP-based
375 method in a repeated fashion is suggested to enhance overall fingermark detection quality when
376 compared to a single treatment and is particularly suitable for weakly-developed fingermarks.
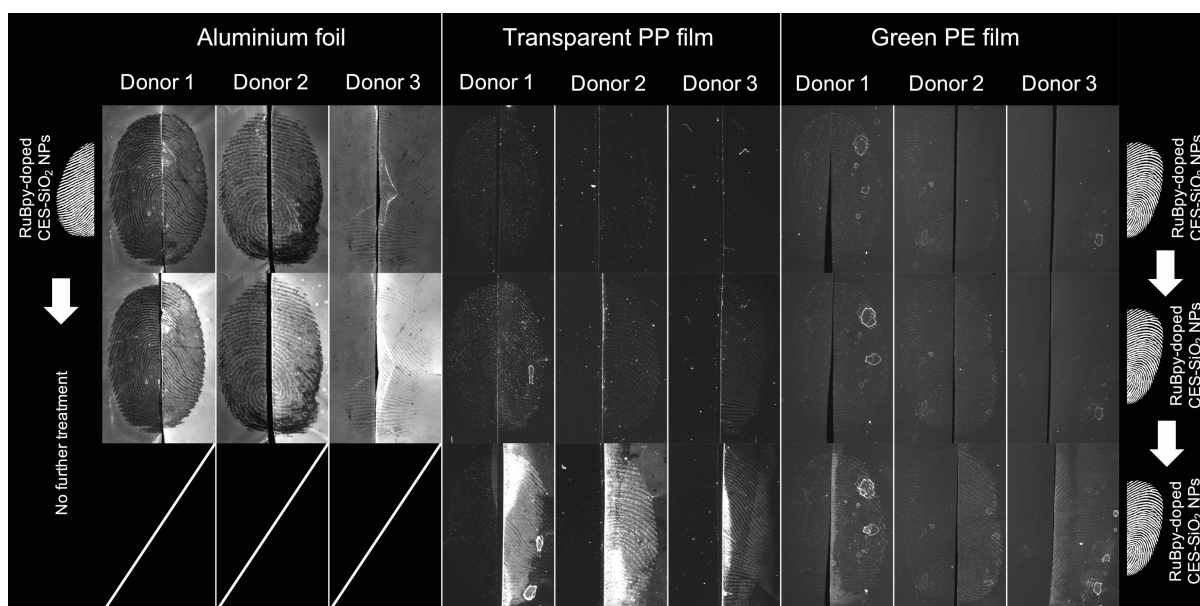
Figure 4: Representative fingermarks from using the optimised RuBpy-doped SiO₂ NP-based method for multiple sequential treatments. On each fingermark, the left half was treated with the NP-based method once while the right half underwent two additional treatments. Fingermarks were three weeks old prior to treatment. The brightness of the fingermark images on transparent PP film and green PE film were increased by 50% and 30% respectively for improved visibility.

As an associated observation, in our previous method optimisation study, it was observed that a 15-min treatment time demonstrated comparable fingermark detection effectiveness to a 5-min treatment. A 5-min immersion time was chosen based on practical considerations [14]. While the results illustrated above might suggest that a 15-min treatment time is superior to a 5-min treatment time, the resulting 15-min treatment was indeed a cumulative period of individual immersions (3 × 5 min). Therefore, the results could not be interpreted as direct comparisons between two single treatments (i.e., 5 min vs 15 min).

3.2.2 Exploring the limit of multiple treatments

393

394   The above experiment demonstrated the feasibility of re-applying the optimised RuBpy-doped

395   SiO$_2$ NP-based method for latent fingermark detection on the evaluated fingermarks. The limit

396   of the total number of fingermark treatments that could be used successively was then

397   investigated. From a practical viewpoint, the aim was to determine whether successive

398   treatment processes would result in unwanted overdevelopment of enhanced fingermarks.

399   Therefore, using a new colloidal dispersion bath for each treatment, the optimised RuBpy-

400   doped SiO$_2$ NP-based method was applied to develop fingermarks collected from the three

401   donors across the three substrates and for a total of 10 successive treatment cycles.

402

403   Figure 5 illustrates three representative full fingermarks developed from each donor on the

404   three substrates with 10 successive treatment cycles. Across the evaluated fingermark

405   specimens on aluminium foil, reverse (negative) development of fingermarks was observed

406   with multiple treatments. In the illustrated example fingermark, it was noted that the first

407   fingermark development was reversed with the NP deposited on the background. In the next

408   four treatment cycles (cycles two to five), the extent of background development increased

409   with only limited NP deposition on the fingermark ridges, before heavy background staining

410   started to produce overdeveloped fingermarks after the sixth fingermark treatment cycle. As

411   observed in the subsequent treatment cycles, the extent of staining of the NPs on aluminium

412   foil increased and caused the complete deposition of a NP layer over the initially developed

413   fingermark ridges leading to a reduction in ridge contrast. The apparent overdevelopment of

414   the fingermark on aluminium foil was noted after the fifth treatment cycle using the SiO$_2$ NP-

415   based method. No fingermark ridge detail was able to be visualised after the eighth treatment

416   cycle on this substrate.
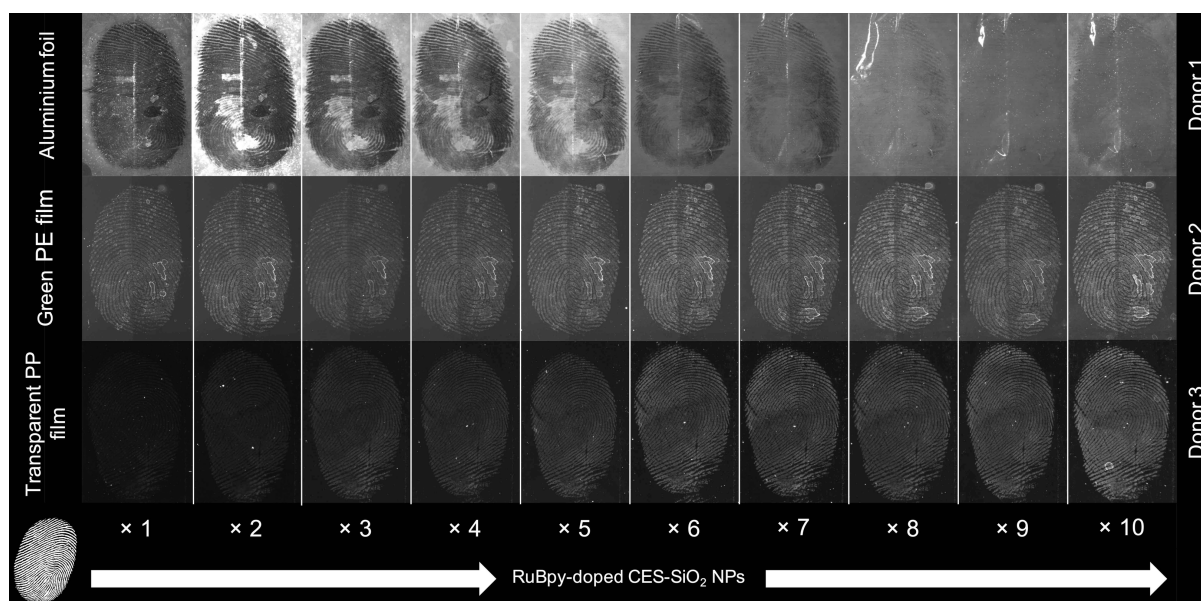
Figure 5: Representative fingermarks from using the RuBpy-doped SiO₂ NP-based method for multiple treatments with a total of 10 treatment cycles. Fingermarks were 10 months old prior to treatment.

For the fingermarks evaluated across the three donors on transparent PP and green PE films that were treated using 10 successive treatment cycles, the overall detection quality was satisfactory. In general, fingermark detection quality improved gradually with the subsequent treatments using the optimised RuBpy-doped SiO_2 NP-based method across the 10 treatment cycles. Increases in fingermark detection quality (e.g., ridge clarity and ridge detail) were more significant across the first five consecutive treatment cycles; improvements in detection quality became less noticeable across the subsequent treatment cycles. No overdevelopment of fingermarks or background staining was observed in the evaluated fingermarks from the 10 fingermark treatment cycles on these two substrates.

On the example fingermark illustrated on the green PE film collected from donor 2 (a strong donor), clear and well-developed ridge detail was obtained after the first fingermark treatment. With the subsequent fingermark treatment cycles, no significant improvement of fingermark detection quality was observed (as most of the fingermark ridge detail was successfully developed after the first treatment). However, no overdevelopment of fingermark ridges or noticeable background staining was prompted from the 10 consecutive fingermark treatment cycles. While a certain degree of overdevelopment was expected on fingermarks from a strong donor after multiple treatment cycles, the absence of this is a desirable trait for the technique.

440 The illustrated fingermark developed on the transparent PP film in Figure 6 was collected from
441 donor 3 (a weak donor) and it was evident that the fingermark was only weakly developed after
442 the first treatment cycle. With the use of the subsequent treatment cycles, the overall
443 fingermark development quality gradually increased. Clearly visible ridge detail (including
444 level 3 ridge detail) was developed after the sixth fingermark treatment cycle.

446 From a practical perspective, it would not be reasonable to process an item for 10 treatment
447 cycles. However, the deliberate and excessive application of treatment cycles in this proof-of-
448 concept experiment demonstrated some favourable traits for the optimised RuBpy-doped SiO_2
449 NP-based method. Based on the evaluated fingermarks, it was demonstrated that the multiple-
450 treatment approach has the ability to significantly improve fingermark detection quality for
451 fingermarks from weaker fingermark donors (as shown with the illustrated fingermark on
452 transparent PP film) and with a low tendency for overdevelopment of treated fingermarks (as
453 shown via the illustrated fingermark on green PE film), particularly for the two plastic
454 substrates tested (PP and PE).

456 A combination of these favourable features for fingermark development—increased
457 enhancement quality with minimal background interference—using the multiple-treatment
458 approach could potentially be advantageous in casework scenarios. As natural fingermark
459 depositions on different items are expected to vary significantly in an operational setting,
460 multiple fingermark treatments using routine methods such as CAF would cause uncontrollable
461 heavy background interference across substrate surfaces. A general trend was that the
462 difference in fingermark detection quality between a strong and a weak donor diminished after
463 multiple treatments. The multiple-treatment approach could potentially be a reliable route to
464 develop fingermarks on non-porous surfaces until desirable enhancement is achieved, without
465 a high risk of overdevelopment.

467 Conclusive remarks regarding the casework application of this proposed multiple-treatment
468 approach cannot be made from this preliminary study; a comparison study with routine
469 detection methods will be needed. Furthermore, it was observed that fingermark enhancement
470 was only able to be achieved via the use of new colloidal dispersion in each successive
471 treatment. No enhancement in detection quality was offered from using the same colloidal
472 dispersion in subsequent treatments.

3.3   Spray application of the nanoparticle-based reagent

As a new fingermark detection method, the RuBpy-doped SiO_2 NPs had been modified and optimised for application in a conventional laboratory setting. Throughout our series of research, the overall practicality of the technique remained an important consideration. Application parameters such as the reduction of NP concentration in the colloidal dispersion and the incorporation of a shaking incubator into the treatment process were both improvements that resulted from applying a practical viewpoint.

To investigate the feasibility of the optimised RuBpy-doped SiO_2 NP-based method for potential casework implementation by end-users, the applicability of the technique outside a conventional laboratory setting was considered. Following the procedure detailed in Section 2.2.4, the water-based NP reagent was applied as a spray to detect latent fingermarks on the three test substrates. This was done in a way that would mimic the treatment of fixed vertical surfaces at a crime scene (for example).

3.3.1 Proof-of-concept spray application for latent fingermark detection

On the fingermarks collected from the three donors on the three test substrates, the optimised RuBpy-doped SiO_2 NP-based method was applied as a spray for fingermark detection. Figure 6 illustrates representative fingermarks treated using the NP-based reagent as a spray. Fingermarks were split in halves for the purpose of subsequent treatment. Across all the evaluated fingermarks, visible ridge detail and good ridge development were observed from the spray-treatment approach.
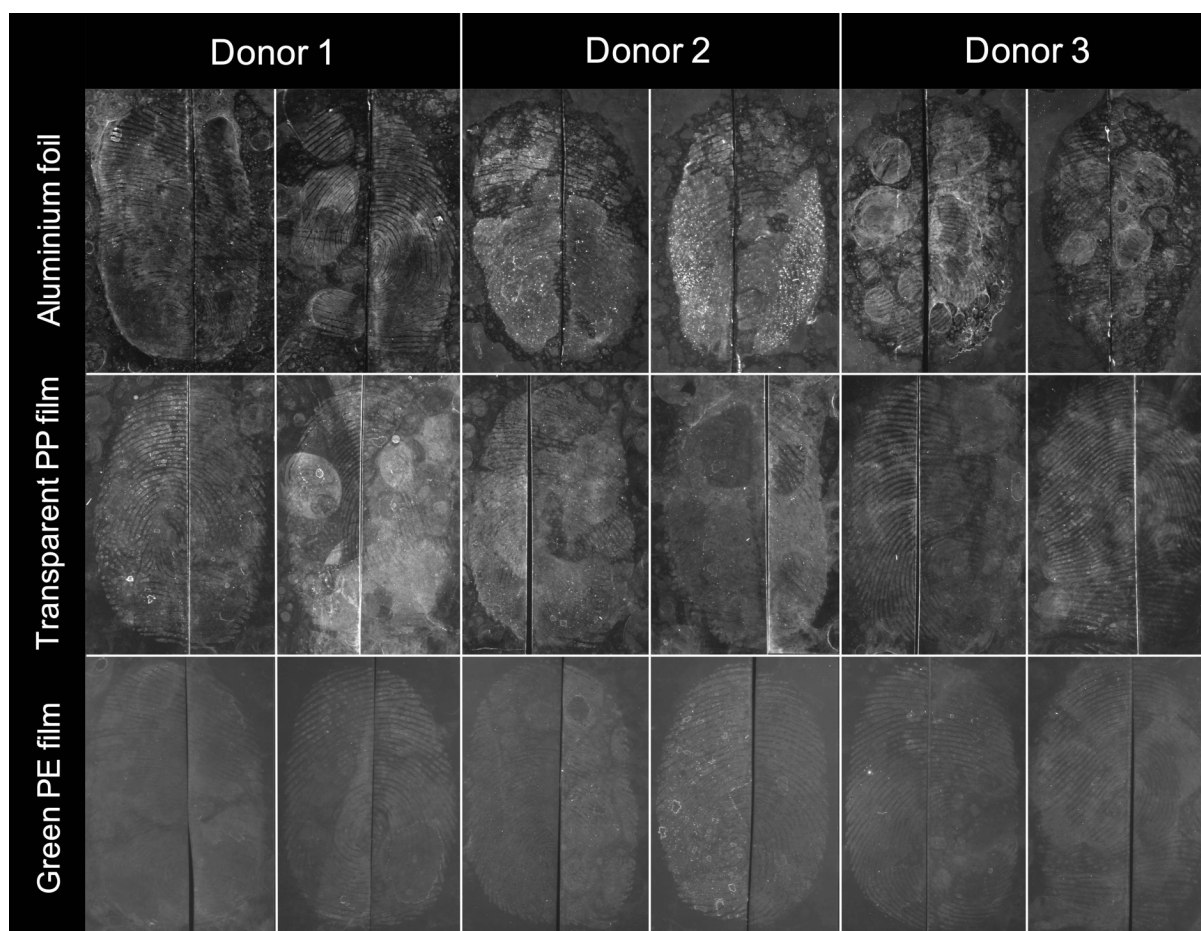
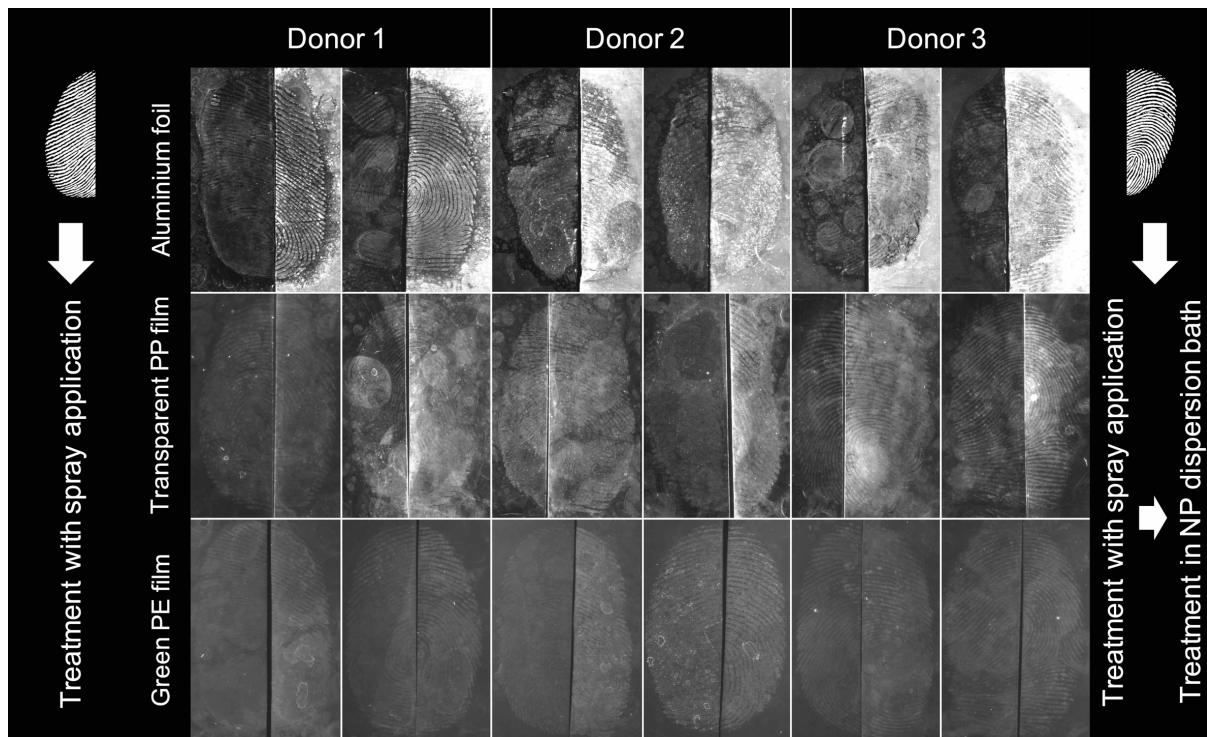*Figure 6: Example fingermarks treated using the optimised RuBpy-doped SiO₂ NP-based method as a spray. Fingermark specimens were one month old prior to treatment. The brightness of all fingermark images illustrated in this figure were increased by 30% for improved visibility.*

To assess the ability to subsequently enhance fingermarks detected via spray application of the NP-based reagent, half of the treated fingermarks in the above experiment underwent treatment using the SiO₂ NP-based method in a colloidal dispersion bath (i.e., fingermark treatment with a 40°C bath with the incorporation of the shaking incubator as per the optimised laboratory-based process). Figure 7 depicts direct comparisons between the fingermarks treated via spray application of the NPs (left halves) and the fingermarks treated using the NP spray followed by the NP bath (right halves). Across the evaluated fingermarks, it was observed that both the fingermark ridge detail and ridge clarity were improved by the subsequent treatment using the NP-based method in a dispersion bath. However, the subsequent treatment bath was not able to remove or reduce the extent of background staining on the fingermarks that resulted from the preceding spray application.

Figure 7: Representative examples from direct comparisons between the fingermark halves treated via spray application of the NPs (left halves) and the fingermarks treated using the NP spray followed by the NP bath (right halves). Fingermark specimens were one month old prior to treatment. The brightness of all images illustrated in this figure were increased by 30% for improved fingermark visibility.

3.3.2 Refinement of spray application parameters

It was indicated that, from the above proof-of-concept experiment, using the optimised RuBpy-doped CES-SiO$_2$ NP-based reagent as a spray is feasible for latent fingermark detection. The overall fingermark detection quality on the evaluated fingermarks was, in fact, better than anticipated. The encouraging preliminary results meant that refinement of the application parameters was needed for a better assessment of the spray application method. A more established spray application procedure was required to obtain a deeper insight into this NP-based treatment approach for latent fingermark detection. From a practical viewpoint, it was desirable to consider an application time for effective fingermark detection. In other words, it was necessary to determine a threshold spray treatment time that would detect fingermarks with "traces of development" visible upon on-site visualisation (fingermark "screening").

533 To determine an adequate application time for the spray-treatment approach, fingermarks
534 collected from the three donors on the three test substrates were treated and the effectiveness
535 of three different durations of treatment (spraying) time—1 min, 2 min and 3 min—are
536 compared in Figure 8. It was observed that, across the evaluated fingermarks, traces of
537 fingermark ridge detail were able to be detected with all three tested treatment times. A 3-min
538 treatment time was judged to provide superior fingermark detection quality in comparison to
539 1-min and 2-min treatment times. On fingermarks from the two stronger donors (donors 1
540 and 2), the effect of various treatment times on fingermark detection quality was not substantial.
541 For the weak donor (donor 3), it was concluded that the fingermarks treated using a 1-min
542 spray application demonstrated inferior fingermark detection quality (e.g., extent of ridge
543 development and ridge clarity) in comparison to the fingermarks treated using a 2- and 3-min
544 treatment time. The above results illustrated a general trend that, as expected, fingermark
545 detection quality increased when treatment (spraying) time increased. This agreed with the
546 trend demonstrated when the RuBpy-doped CES-SiO$_2$ NP-based reagent was applied as a
547 colloidal dispersion bath [14].
548
549 While better fingermark detection quality was produced with the two longer treatment times
550 (2 min and 3 min), it was encouraging that the fingermark evaluation from this experiment
551 demonstrated that some fingermark detail was able to be detected with a 1-min application time
552 using the NP spray treatment. The ability to detect latent fingermarks in a relatively short time
553 is a potentially useful trait from a practical viewpoint. For example, when some development
554 is indicated, further spray application at that location can be carried out for further enhancement.
555 Based on the evaluated fingermarks, a 2-min treatment could be utilised as a reference
556 application time for using the spray treatment to produce detectable fingermarks with sufficient
557 development for initial visualisation (screening).
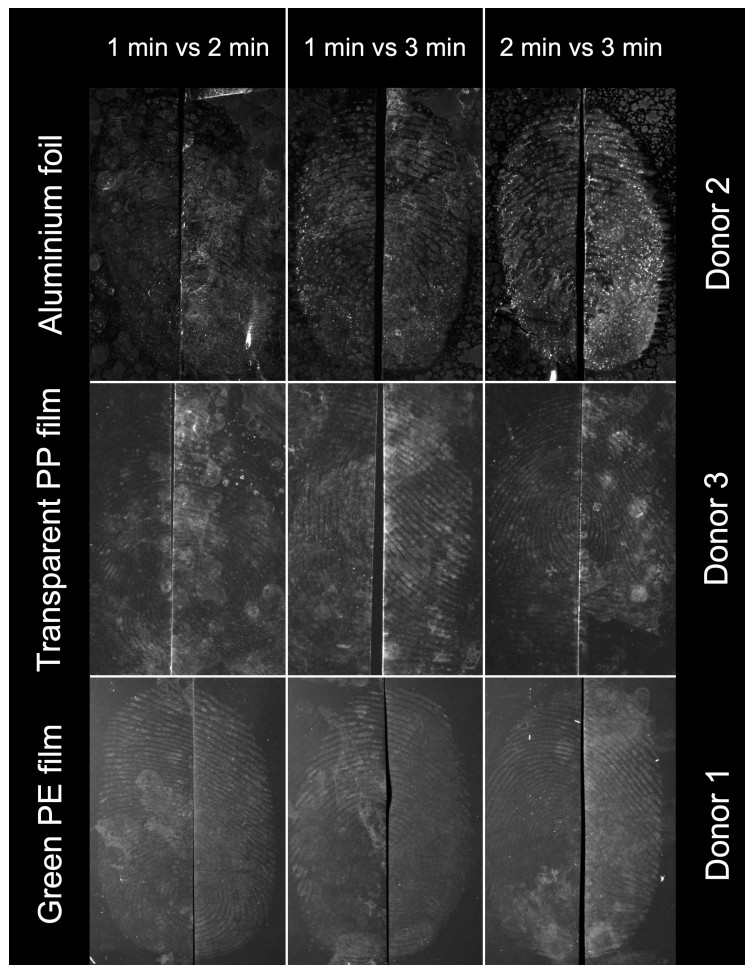
Figure 8: Representative direct fingermark comparisons of fingermark detection quality treated using the NP-based reagent as a spray with the three evaluated treatment times—1 min, 2 min and 3 min. The brightness of the fingermark images for donor 3 on transparent PP film and the brightness and contrast of the fingermark images for donor 1 on green film were increased by 50% for improved visibility.

Compared to the experiment presented in the previous section (Section 3.3.1), a modified approach for a more effective "rinse" step after the NP spray application was introduced. Using a trigger spray bottle, a larger amount of Type 1 ultrapure water was sprayed onto the NP spray-treated fingermarks. Twenty spray pumps of water (approximately 18 mL) were used on a 50×30 cm area over 1 min. As a result of the modified rinse step, the extent of background staining after the spray treatment was significantly less across the three test substrates. The developed ridge detail was not obscured by background NP staining; a sufficient amount of water in the rinse step ensured the effective removal of background NPs.

573 From the above, a refined application protocol for using the optimised RuBpy-doped CES-
574 SiO$_2$ NP-based reagent as a spray is suggested below. Note that no in-depth optimisation was
575 performed in this proof-of-concept study; the suggested procedure is provided as a general
576 indication only. Figure 9 illustrates the spray-treatment approach using the NPs to detect latent
577 fingermarks on fixed surfaces at a crime scene:

578   1. Apply the optimised RuBpy-doped CES-SiO$_2$ NP-based reagent as a spray to the
579   surface of interest.
580   2. If there is an indication of fingermark development, additional treatment time (e.g.,
581   2 min) can be utilised to increase fingermark detection quality. Treated fingermarks are
582   then left to "develop" for an additional 1 min.
583   3. Treated surfaces are then sprayed with water to remove background NP droplets.
584   4. The quality of developed fingermarks can be assessed with the naked eye (e.g., a
585   portable forensic light source with 450 nm excitation, paired with orange goggles).

586
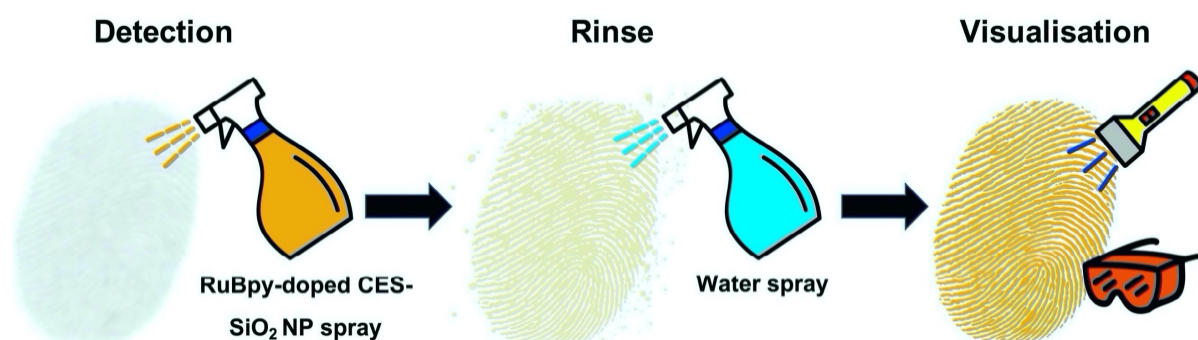
587

588 *Figure 9: Schematic diagram illustrating the suggested application protocol using the*
589 *optimised RuBpy-doped CES-SiO$_2$ NP-based reagent as a spray to detect latent fingermarks.*

590

591 The proof-of-concept study presented in this section demonstrated the feasibility of utilising
592 the optimised RuBpy-doped SiO$_2$ NP-based reagent as a spray to detect latent fingermarks. As
593 a new application approach, it was demonstrated that, when traces of fingermark development
594 were detected by the use of spray treatment, further enhancement of the detected fingermarks
595 was achievable via subsequent treatment using the NP-based method as a colloidal dispersion
596 bath. Therefore, it is suggested that a combination of treatments using the spray application
597 and the NPs as a colloidal dispersion bath could potentially be a useful application route for
598 casework scenarios (e.g., on-site spray application followed by laboratory-based treatment
599 using a colloidal dispersion bath). Figure 10 depicts example fingermarks treated using the NP-
600 based method in a colloidal dispersion bath with two treatment cycles, in comparison with

601   fingermarks treated using the spray-treatment approach followed by the NP bath. It was

602   observed that the difference in overall fingermark detection quality between the two treatment

603   sequences was not significant. Both sequences were able to develop fingermarks with

604   identifiable ridge detail. In the representative fingermarks illustrated, the developed fingermark

605   ridges treated using two cycles in a colloidal dispersion bath were slightly more homogeneous

606   than for the respective half impressions. Background staining was also more prominent on the

607   fingermarks treated using the spray application followed by the colloidal dispersion bath.

608
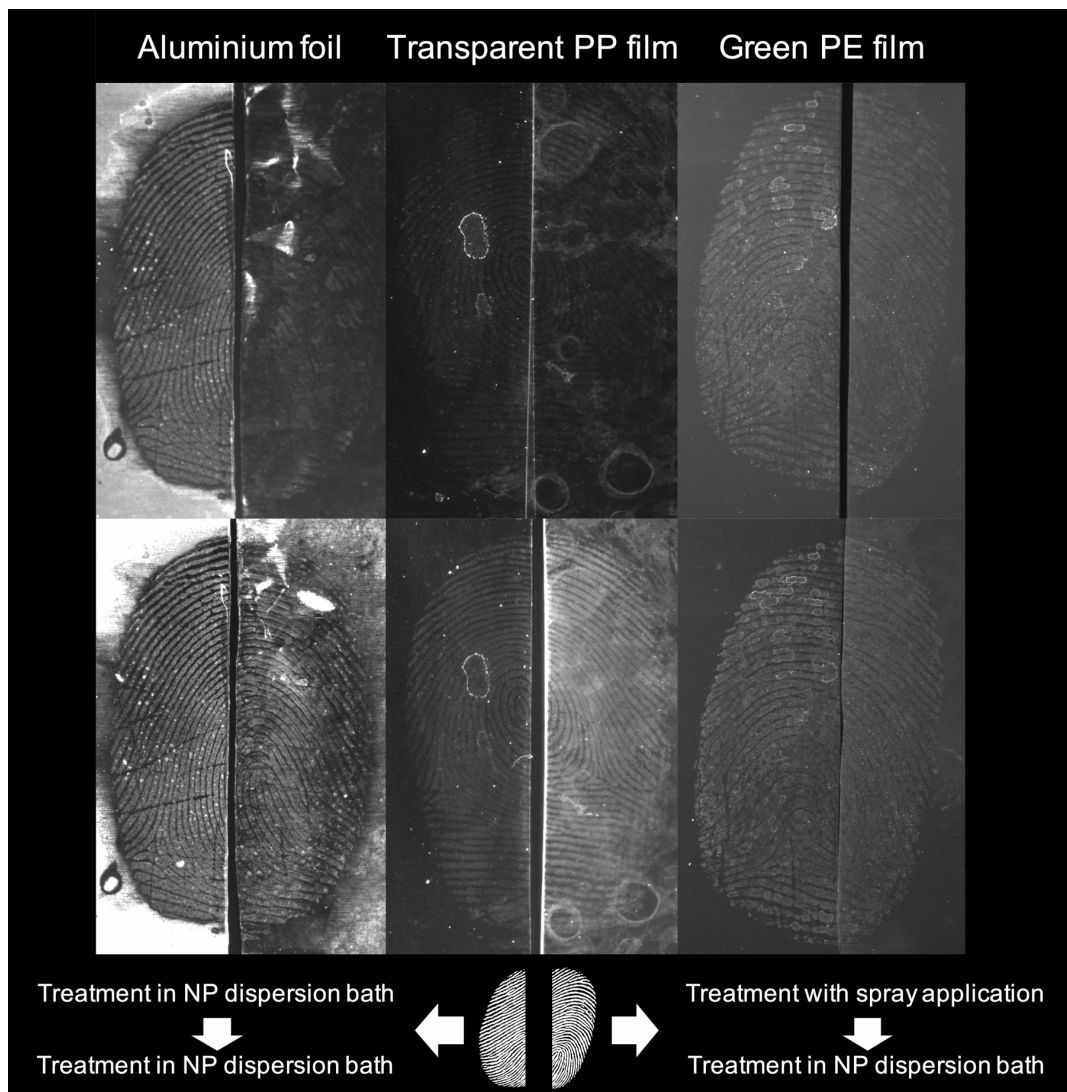
610   *Figure 10: Representative fingermarks illustrating direct comparisons of fingermarks treated*

611   *using two different treatment sequences. Left fingermark halves were developed using the NP-*

612   *based method in a colloidal dispersion bath with two treatment cycles, while right fingermark*

613   *halves were developed using the spray treatment followed with a treatment using the NP-based*

614   *method in a bath. Fingermarks were one month old prior to treatment.*

As an important remark on the spray-treatment approach, NPs are materials with unique and sometimes unexpected properties; as such, safety remains one of the major concerns when NPs are used for various applications [54]. In particular, inhalation of NPs during application poses a significant health concern for end-users. While there has not been a specific study conducted to assess the toxicity of the RuBpy-doped CES-SiO$_2$ NPs, it is believed that the current application route for the optimised NP-based method in a dispersion bath is relatively safe to use. This is based on the fact that the NPs are suspended in water and are, therefore, extremely unlikely to become "airborne" during a treatment process. However, the spray application of the NP-based reagent, as conducted in this study inside a glove box, would need to be evaluated from a work health and safety perspective before it could be considered for operational use.

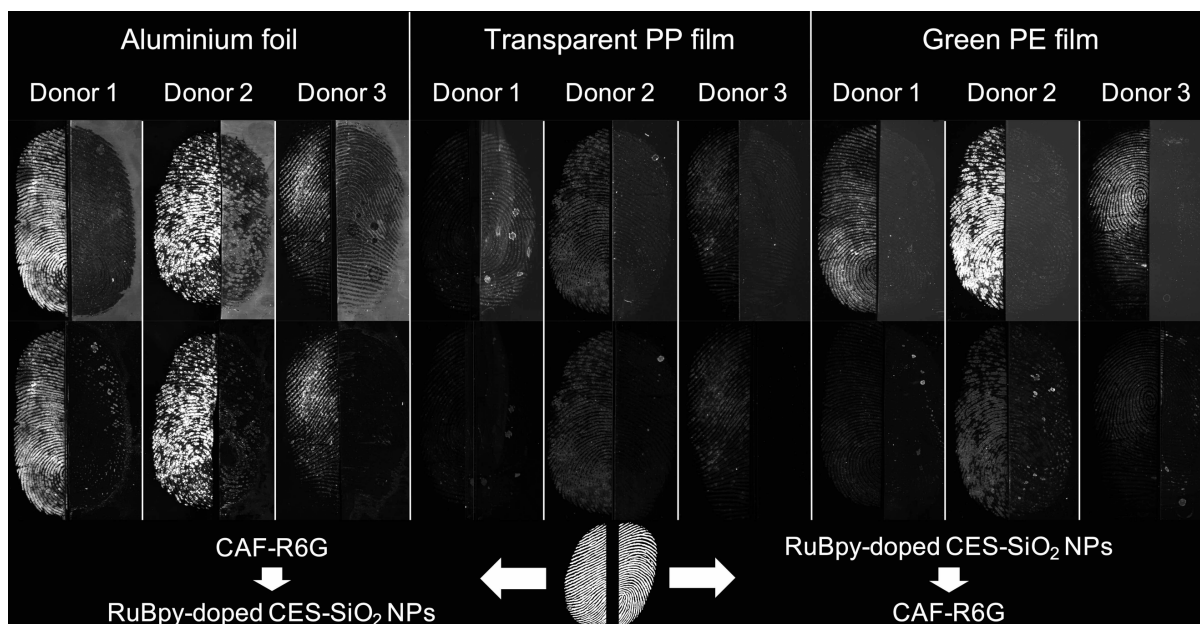## 3.4   Compatibility with two-step cyanoacrylate fuming

As outlined in the IFRG research guidelines, the compatibility of novel fingermark reagents with routine techniques should be tested [47]. Therefore, the optimised RuBpy-doped CES-SiO$_2$ NP-based method was applied for fingermark development in sequence with a benchmark method, CAF-R6G. Figure 11 illustrates representative fingermarks obtained when the optimised NP-based method was used in sequence with CAF-R6G. In line with the other proof-of-concept experiments described in this study, fingermark specimens were collected from the same three donors across the same three substrates. On the evaluated fingermarks, it was observed that fingermark detection quality was not improved in any of the fingermarks by either sequence (i.e., NP treatment before or after CAF-R6G; Figure 11).

For the "SiO$_2$ NP-based method $\rightarrow$ CAF-R6G" sequence, it was evident that when the NP-based method was applied before CAF-R6G, it had a detrimental effect on the performance of CAF. It was observed that no homogeneous ridges were obtained after CAF application. It is known that CAF is less effective on items that have been wet as certain water-soluble fingermark components are believed to be important for the effective initiation of the CA polymerisation process [55]. While all fingermark specimens were dried prior to CAF treatment, the preceding treatment using the water-based SiO$_2$ NP-based method was judged to be detrimental to the subsequent CAF process. Therefore, the use of CAF on fingermarks already treated using the SiO$_2$ NP-based method—with the current water-based detection bath—is not recommended.

On the evaluated fingermarks treated in the "CAF-R6G → SiO₂ NP-based method" sequence, the use of the NPs had minimal effect and did not increase fingermark detection quality on aluminium foil and transparent PP film. No significant impact was observed on the fingermark ridge detail developed from the CAF-R6G process. On green PE film, a decrease in luminescence intensity was observed along the fingermark ridges. Although no conclusive explanation can be drawn from this observation, a possible cause could be a "leakage" and "dilution" of R6G dye molecules during the SiO₂ NP-treatment process. No decrease in fingermark luminescence was observed on aluminium foil and transparent PP film and, as such, further investigations would be required to provide a more detailed insight.

On the evaluated fingermarks, the development of ridge detail was judged to be fairly complete after treatment using CAF-R6G. This could explain the overall low effectiveness when the SiO₂ NP-based method was subsequently applied. Another probable cause could be the mere incompatibility of NP deposition onto CA-developed ridges (i.e., there is a lack of desirable interaction for further fingermark enhancement between the surface-functionalised SiO₂ NPs

671   and the polycyanoacrylate formed along CA-developed fingermark ridges). The staining of the

672   aluminium foil by the NPs, as observed throughout this research and previous studies, appeared

673   to be homogeneous across the substrate surface. It was suggested in the previous study that the

674   CES-SiO$_2$ NPs may chemically interact with aluminium foil [15]. However, as observed in this

675   experiment, no background staining appeared on aluminium foil when the SiO$_2$ NP-based

676   method was applied after CAF-R6G. This suggests that the behaviour of the RuBpy-doped

677   CES-SiO$_2$ NPs is significantly impacted by prior CA fuming of the substrates.

678

679   From the above proof-of-concept experiment, the optimised RuBpy-doped CES-SiO$_2$ NP-

680   based method is suggested to be incompatible with CAF for latent fingermark detection. The

681   major limitation is that the water-based treatment using the NPs significantly hinder the

682   detection effectiveness of subsequent CAF development. Whereas, applying the NPs after CAF

683   failed to improve the quality of developed fingermarks.

684

685   4. <u>Conclusions</u>

686

687   This study investigated a series of proof-of-concept experiments that utilised RuBpy-doped

688   CES-SiO$_2$ NPs to detect latent fingermarks on non-porous surfaces. By repeated application of

689   the optimised RuBpy-doped CES-SiO$_2$ NP-based method, overall fingermark detection quality

690   increased significantly across the evaluated fingermarks. While an in-depth study will be

691   required to further assess the multiple-treatment approach using the NP-based method, it is

692   suggested that such characteristics for fingermark enhancement from successive treatments

693   (enhancement of fingermarks without a high risk of overdevelopment) could be advantageous

694   to develop fingermarks until desirable development quality is achieved. The reusability of the

695   NP colloidal dispersion for multiple treatments was examined and it was concluded that

696   fingermark enhancement is only effective with the use of freshly-prepared colloidal dispersion

697   for each treatment cycle.

698

699   To investigate the application of the optimised RuBpy-doped CES-SiO$_2$ NP-based reagent for

700   potential casework implementation, the NP-based reagent was applied as a spray to detect

701   latent fingermarks on non-porous surfaces (aluminium foil, transparent PP film and green PE

702   film). The spray-treatment approach demonstrated that it was feasible to detect the fingermarks

703   evaluated in this study, with good fingermark ridge detail obtained. Upon refinement of

704 application parameters, traces of fingermark development were able to be detected with a 1-min
705 application (spraying) time. This observation was deemed encouraging from a practical
706 standpoint. Moreover, it was determined that further enhancement of "spray-detected"
707 fingermarks can be accomplished by subsequent treatment using the RuBpy-doped CES-SiO$_2$
708 NP-based reagent in a colloidal dispersion bath.

709

710 Furthermore, the compatibility of the optimised RuBpy-doped CES-SiO$_2$ NP-based method
711 with a benchmark fingermark detection technique was evaluated. The NP-based method was
712 applied in sequence with CAF-R6G for latent fingermark detection. The results showed that
713 the two techniques are not compatible for application in a detection sequence.

714

715 The proof-of-concept experiments presented in this study demonstrated that the optimised
716 RuBpy-doped CES-SiO$_2$ NP-based reagent is highly versatile for latent fingermark detection.
717 While encouraging results were observed throughout the experiments, it should be emphasised
718 that more comprehensive assessments will be required for any of the evaluated treatment
719 approaches (e.g., multiple treatments and spray application) to be considered for operational
720 implementation. In particular, the potential spray application of the NP-based reagent would
721 need to the evaluated from a work health and safety perspective before it could be further
722 considered.

723

724 **Ethics statement**

725

726 The collection and processing of fingermark specimens for this study were approved by the
727 Western Sydney University Human Research Ethics Committee (approval numbers H10909
728 and H13483). All fingermark donors read, understood and signed consent forms prior to
729 participating in the study.

References

[1] G. Schmid, The Nature of Nanotechnology, in: H. Fuchs, M. Grätzel, H. Krug, G. Schmid, V. Vogel, R. Waser (Eds.), Nanotechnology, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010, pp. 3-39.

[2] L. Wang, C. Yang, W. Tan, Dual-Luminophore-Doped Silica Nanoparticles for Multiplexed Signaling, Nano Letters 5(1) (2005) 37-43.

[3] L.F. de Oliveira, K. Bouchmella, A.S. Picco, L.B. Capeletti, K.A. Gonçalves, J.H.Z. dos Santos, J. Kobarg, M.B. Cardoso, Tailored Silica Nanoparticles Surface to Increase Drug Load and Enhance Bactericidal Response, Journal of the Brazilian Chemical Society 28 (2017) 1715-1724.

[4] L. Torrisi, N. Restuccia, Laser-Generated Au Nanoparticles for Bio-Medical Applications, IRBM 39(5) (2018) 307-312.

[5] E. Zhang, R. Xing, S. Liu, Y. Qin, K. Li, P. Li, Advances in chitosan-based nanoparticles for oncotherapy, Carbohydrate Polymers 222 (115004) (2019) 1-12.

[6] L.D. Carlos, R.A. Sá Ferreira, V. de Zea Bermudez, Organic–Inorganic Hybrids for Light-Emitting Devices and Integrated Optics, in: L. Merhari (Ed.), Hybrid Nanocomposites for Nanotechnology: Electronic, Optical, Magnetic and Biomedical Applications, Springer, New York, NY, 2009, pp. 509-586.

[7] Y. Zhou, Y. Chen, H. Wang, C.P. Wong, Creation of a multilayer aluminum coating structure nanoparticle polyimide filler for electronic applications, Materials Letters 119 (2014) 64-67.

[8] B.D. Keller, N. Ferralis, J.C. Grossman, Rethinking Coal: Thin Films of Solution Processed Natural Carbon Nanoparticles for Electronic Devices, Nano Letters 16(5) (2016) 2951-2957.

[9] A. Bécue, A.A. Cantú, Fingermark Detection Using Nanoparticles, in: R.S. Ramotowski (Ed.), Lee and Gaensslen's Advances in Fingerprint Technology, 3rd ed., CRC Press, Boca Raton, FL, 2012, pp. 307-380.

758 [10] S. Moret, A. Bécue, C. Champod, Nanoparticles for fingermark detection: an insight into the reaction mechanism, Nanotechnology 25 (455502)(42) (2014) 1-10.

760 [11] S. Moret, A. Bécue, C. Champod, Functionalised silicon oxide nanoparticles for fingermark detection, Forensic Science International 259 (2016) 10-18.

762 [12] B.J. Theaker, K.E. Hudson, F.J. Rowell, Doped hydrophobic silica nano- and micro-particles as novel agents for developing latent fingerprints, Forensic Science International 174(1) (2008) 26-34.

765 [13] L. Liu, S.K. Gill, Y. Gao, L.J. Hope-Weeks, K.H. Cheng, Exploration of the use of novel SiO_2 nanocomposites doped with fluorescent Eu^{3+}/sensitizer complex for latent fingerprint detection, Forensic Science International 176(2) (2008) 163-172.

768 [14] P.L.T. Lee, F.K. Kanodarwala, C. Lennard, X. Spindler, V. Spikmans, C. Roux, S. Moret, Latent fingermark detection using functionalised silicon oxide nanoparticles: Method optimisation and evaluation, Forensic Science International 298 (2019) 372-383.

772 [15] P.L.T. Lee, F.K. Kanodarwala, C. Lennard, X. Spindler, V. Spikmans, C. Roux, S. Moret, Latent fingermark detection using functionalised silicon oxide nanoparticles: Optimisation and comparison with cyanoacrylate fuming, Forensic Science International 315 (110442) (2020) 1-12.

776 [16] S. Chadwick, S. Moret, N. Jayashanka, C. Lennard, X. Spindler, C. Roux, Investigation of some of the factors influencing fingermark detection, Forensic Science International 289 (2018) 381-389.

779 [17] M. de la Hunty, S. Moret, S. Chadwick, C. Lennard, X. Spindler, C. Roux, Understanding physical developer (PD): Part I—Is PD targeting lipids?, Forensic Science International 257 (2015) 481-487.

782 [18] M. de la Hunty, S. Moret, S. Chadwick, C. Lennard, X. Spindler, C. Roux, Understanding Physical Developer (PD): Part II—Is PD targeting eccrine constituents?, Forensic Science International 257 (2015) 488-495.

785 [19] R.S. Ramotowski, Metal Deposition Methods, in: R.S. Ramotowski (Ed.), Lee and
786   Gaensslen's Advances in Fingerprint Technology, 3rd ed., CRC Press, Boca Raton, FL,
787   2012, pp. 55-82.

788 [20] F.K. Kanodarwala, S. Moret, X. Spindler, C. Lennard, C. Roux, Nanoparticles used for
789   fingermark detection—A comprehensive review, Wiley Interdisciplinary Reviews:
790   Forensic Science 1 (e1341)(5) (2019) 1-41.

791 [21] G. Saunders, Multimetal deposition method for latent fingerprint development, 74th
792   Conference of the International Association for Identification, Pensacola, FL, 1989.

793 [22] B. Schnetz, P. Margot, Technical note: latent fingermarks, colloidal gold and
794   multimetal deposition (MMD): Optimisation of the method, Forensic Science
795   International 118(1) (2001) 21-28.

796 [23] E. Stauffer, A. Bécue, K.V. Singh, K.R. Thampi, C. Champod, P. Margot, Single-metal
797   deposition (SMD) as a latent fingermark enhancement technique: An alternative to
798   multimetal deposition (MMD), Forensic Science International 168(1) (2007) e5-e9.

799 [24] P. Durussel, E. Stauffer, A. Bécue, C. Champod, P. Margot, Single-metal deposition:
800   Optimization of this fingermark enhancement technique, Journal of Forensic
801   Identification 59(1) (2009) 80-96.

802 [25] A. Bécue, A. Scoundrianos, S. Moret, Detection of fingermarks by colloidal gold
803   (MMD/SMD)—beyond the pH 3 limit, Forensic Science International 219(1–3) (2012)
804   39-49.

805 [26] S. Moret, A. Bécue, Single-Metal Deposition for Fingermark Detection—A Simpler
806   and More Efficient Protocol, Journal of Forensic Identification 65(2) (2015) 118-137.

807 [27] E.R. Menzel, S.M. Savoy, S.J. Ulvick, K.H. Cheng, R.H. Murdock, M.R. Sudduth,
808   Photoluminescent Semiconductor Nanocrystals for Fingerprint Detection, Journal of
809   Forensic Sciences 45(3) (2000) 545-51.

810 [28] E.R. Menzel, M. Takatsu, R.H. Murdock, K. Bouldin, K.H. Cheng, Photoluminescent
811   CdS/Dendrimer Nanocomposites for Fingerprint Detection, Journal of Forensic
812   Sciences 45(4) (2000) 770-3.

813 [29] A. Bécue, S. Moret, C. Champod, P. Margot, Use of quantum dots in aqueous solution
814   to detect blood fingermarks on non-porous surfaces, Forensic Science International
815   191(1–3) (2009) 36-41.

816 [30] J. Dilag, H. Kobus, A.V. Ellis, Cadmium sulfide quantum dot/chitosan nanocomposites
817   for latent fingermark detection, Forensic Science International 187(1–3) (2009) 97-102.

818 [31] D. Fernandes, M.J. Krysmann, A. Kelarakis, Carbon dot based nanopowders and their
819   application for fingerprint recovery, Chemical Communications 51(23) (2015) 4902-
820   4905.

821 [32] J. Dilag, H. Kobus, A.V. Ellis, CdS/polymer nanocomposites synthesized via surface
822   initiated RAFT polymerization for the fluorescent detection of latent fingermarks,
823   Forensic Science International 228(1–3) (2013) 105-114.

824 [33] J. Dilag, H. Kobus, Y. Yu, C.T. Gibson, A.V. Ellis, Non-toxic luminescent carbon
825   dot/poly(dimethylacrylamide) nanocomposite reagent for latent fingermark detection
826   synthesized via surface initiated reversible addition fragmentation chain transfer
827   polymerization, Polymer International 64(7) (2015) 884-891.

828 [34] R. Ma, E. Bullock, P. Maynard, B. Reedy, R. Shimmon, C. Lennard, C. Roux, A.
829   McDonagh, Fingermark detection on non-porous and semi-porous surfaces using
830        $NaYF_4$:Er,Yb upconverter particles, Forensic Science International 207(1) (2011) 145-
831   149.

832 [35] R. Ma, R. Shimmon, A. McDonagh, P. Maynard, C. Lennard, C. Roux, Fingermark
833   detection on non-porous and semi-porous surfaces using YVO_4:Er,Yb luminescent
834   upconverting particles, Forensic Science International 217(1–3) (2012) e23-e26.

835 [36] S.P. Tiwari, K. Kumar, V.K. Rai, Latent fingermarks detection for La_2O_3:Er^{3+}/Yb^{3+}
836   phosphor material in upconversion emission mode: A comparative study, Journal of
837   Applied Physics 118 (183109)(18) (2015) 1-7.

838 [37] A. Kumar, S.P. Tiwari, A.K. Singh, K. Kumar, Synthesis of Gd_2O_3:Ho^{3+}/Yb^{3+}
839   upconversion nanoparticles for latent fingermark detection on difficult surfaces,
840   Applied Physics B 122 (190)(7) (2016) 1-10.

841 [38] P. Du, P. Zhang, S.H. Kang, J.S. Yu, Hydrothermal synthesis and application of Ho^{3+}-
842 activated $NaYbF_4$ bifunctional upconverting nanoparticles for in vitro cell imaging and
843 latent fingerprint detection, Sensors and Actuators B: Chemical 252 (2017) 584-591.

844 [39] A. Sandhyarani, M.K. Kokila, G.P. Darshan, R.B. Basavaraj, B. Daruka Prasad, S.C.
845 Sharma, T.K.S. Lakshmi, H. Nagabhushana, Versatile core–shell $SiO_2@SrTiO_3:Eu^{3+}$,
846 Li^+ nanopowders as fluorescent label for the visualization of latent fingerprints and anti-
847 counterfeiting applications, Chemical Engineering Journal 327 (2017) 1135-1150.

848 [40] F.K. Kanodarwala, A. Leśniewski, I. Olszowska-Łoś, X. Spindler, I.S. Pieta, C.
849 Lennard, J. Niedziółka-Jönsson, S. Moret, C. Roux, Fingermark detection using
850 upconverting nanoparticles and comparison with cyanoacrylate fuming, Forensic
851 Science International 326 (2021) 110915.

852 [41] W. Huang, X. Li, H. Wang, X. Xu, H. Liu, G. Wang, Synthesis of Amphiphilic Silica
853 Nanoparticles for Latent Fingerprint Detection, Analytical Letters 48(9) (2015) 1524-
854 1535.

855 [42] D. Fernandes, M.J. Krysmann, A. Kelarakis, Carbogenically coated silica nanoparticles
856 and their forensic applications, Chemical Communications 52(53) (2016) 8294-8296.

857 [43] D. Peng, X. Liu, M. Huang, D. Wang, R. Liu, A novel monodisperse $SiO_2@C$-dot for
858 the rapid and facile identification of latent fingermarks using self-quenching resistant
859 solid-state fluorescence, Dalton Transactions 47(16) (2018) 5823-5830.

860 [44] Y.-J. Kim, H.-S. Jung, J. Lim, S.-J. Ryu, J.-K. Lee, Rapid Imaging of Latent
861 Fingerprints Using Biocompatible Fluorescent Silica Nanoparticles, Langmuir 32(32)
862 (2016) 8077-8083.

863 [45] L. Meng, Y. Ren, Z. Zhou, C. Li, C. Wang, S. Fu, Monodisperse silica nanoparticle
864 suspension for developing latent blood fingermarks, Forensic Sciences Research 5(1)
865 (2020) 38-46.

866 [46] I. Olszowska, A. Leśniewski, A. Kelm, I.S. Pieta, A. Siejca, J. Niedziółka-Jönsson,
867 Zinc oxide quantum dots embedded in hydrophobic silica particles for latent
868 fingermarks visualization based on time-gated luminescence measurements, Methods
869 and Applications in Fluorescence 8 (025001)(2) (2020) 1-11.

870   [47]   International Fingerprint Research Group (IFRG), Guidelines for the Assessment of
871   Fingermark Detection Techniques, Journal of Forensic Identification 64(2) (2014) 174-
872   200.

873   [48]   K.J. Farrugia, D. Hunter, C. Wilson, S. Hay, P. Sherriffs, P. Deacon, Further Pseudo-
874   Operational Trials with the Lumicyano Double- and Co-Fuming Process for the
875   Detection of Latent Fingermarks, Journal of Forensic Sciences 65(1) (2020) 248-254.

876   [49]   S. Merrick, S.J. Gardner, V.G. Sears, D.F. Hewlett, An operational trial of ozone-
877   friendly DFO and 1,2-indanedione formulations for latent fingerprint detection, Journal
878   of Forensic Identification 52(5) (2002) 595-605.

879   [50]   N. Nicolasora, R. Downham, R.-M. Dyer, L. Hussey, A. Luscombe, V. Sears, A
880   validation study of the 1,2-indandione reagent for operational use in the UK: Part 2—
881   Optimization of processing conditions, Forensic Science International 288 (2018) 266-
882   277.

883   [51]   N. Nicolasora, R. Downham, L. Hussey, A. Luscombe, K. Mayse, V. Sears, A
884   validation study of the 1,2-indandione reagent for operational use in the UK: Part 1—
885   Formulation optimization, Forensic Science International 292 (2018) 242-253.

886   [52]   N. Porpiglia, S. Bleay, L. Fitzgerald, L. Barron, An assessment of the effectiveness of
887   5-methylthioninhydrin within dual action reagents for latent fingerprint development
888   on paper substrates, Science & Justice 52(1) (2012) 42-48.

889   [53]   D. Peng, X. Liu, M. Huang, R. Liu, Characterization of a Novel Co_2TiO_4 Nanopowder
890   for the Rapid Identification of Latent and Blood Fingerprints, Analytical Letters 51(11)
891   (2018) 1796-1808.

892   [54]   Nanoscience and nanotechnologies: opportunities and uncertainties, The Royal Society,
893   London, United Kingdom, 2004.

894   [55]   C. Champod, C. Lennard, P. Margot, M. Stoilovic, Fingerprints and Other Ridge Skin
895   Impressions, 2nd ed., CRC Press, Boca Raton, FL, 2016.

896