

1 *Proposition of: paper*

2 **Functionalised silicon oxide nanoparticles for**
3 **fingermark detection**

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22 HIGHLIGHTS

- 23 • Synthesis of luminescent and functionalised silicon oxide nanoparticles
- 24 • These nanoparticles regroup all desired properties for fingerprint detection
- 25 • The technique is effective on non-porous substrates
- 26 • The technique performed similarly compared to one-step luminescent cyanoacrylate
- 27 • Silicon oxide nanoparticles are less affected by donor inter-variability

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29

30 **Abstract:**

31 Over the past decade, the use of nanotechnology for fingerprint detection has been attracting
32 a lot of attention. A substantial number of nanoparticle types has thus been studied and
33 applied with varying success. However, despite all efforts, few publications present clear
34 supporting evidence of their superiority over standard and commonly used techniques. This
35 paper focuses on a rarely studied type of nanoparticles that regroups all desired properties for
36 effective fingerprint detection: silicon oxide. These nanoparticles offer optical and surface
37 properties that can be tuned to provide optimal detection. This study explores their potential
38 as a new method for fingerprint detection.

39 Detection conditions, outer functionalisations and optical properties were optimised and a
40 first evaluation of the technique is presented. Dye-doped silicon oxide nanoparticles were
41 assessed against a one-step luminescent cyanoacrylate. Both techniques were compared on
42 natural fingerprints from three donors collected on four different non-porous substrates. On
43 average, the two techniques performed similarly but silicon oxide detected marks with a
44 better homogeneity and was less affected by donor inter-variability. The technique remains to
45 be further optimised and yet silicon oxide nanoparticles already show great promises for
46 effective fingerprint detection.

47

48 **Keywords:** Nanotechnology, luminescence, sensitivity, selectivity, cyanoacrylate, non-
49 porous substrates.

50

51 **1. Introduction**

52 Nanoparticles applied for fingerprint detection are known to offer several advantages over
53 traditional methods [1]. First, their small size may lead to detect marks with a high resolution
54 without risking over-development that can typically arise with conventional techniques such
55 as powder dusting or cyanoacrylate fuming. Second, some nanoparticles possess interesting
56 luminescent properties spread over a broad area of the electromagnetic spectrum ranging
57 from UV to infrared. Conventional luminescence properties, as well as up-conversion can be
58 used to mitigate substrate interferences. Infrared luminescence is also of great interest for
59 problematic surfaces since few materials are optically active in this range of wavelengths [2].
60 Finally, and more importantly, the surface of nanoparticles can be precisely tuned to offer a
61 large panel of potential interaction with fingerprints. By grafting molecules or functional
62 groups onto their surfaces, it becomes possible to specifically target various components of
63 the fingerprint residue, leading to an increased selectivity. Fingerprints left by smokers could
64 thus be distinguished from the marks left by non-smokers [3]. Altogether, these properties
65 show great promises for fingerprint detection, and can lead to an overall increase of both
66 sensitivity and selectivity.

67 Over the past decade, these advantages attracted a lot of attention and a substantial number of
68 nanoparticle types have been studied and applied with varying success. They can be sorted
69 into three categories, i.e. metal, metal oxide and semi-conductors. Gold and silver
70 nanoparticles have been successfully used in techniques such as multi- or single-metal
71 deposition (gold) [4, 5] or physical developer (silver) [6]. Among metal oxides, we can cite
72 titanium dioxide (TiO_2) [7], aluminium oxide (Al_2O_3) [8, 9] or zinc oxide (ZnO) [10]. Metal
73 oxides are generally applied as dried powders, sometimes functionalised with aliphatic chains
74 to increase and favour hydrophobic interactions with greasy components of the fingerprint
75 residue. Quantum dots are the most studied class of semiconductors. They attracted a lot of
76 attention mostly for their uncommon optical properties [11, 12]. This paper does not intend to
77 describe these nanoparticles in extensive details; thorough reviews are available elsewhere
78 [13, 14].

79 However, from a critical viewpoint, none of the nanoparticles studied until now and their
80 subsequent applications entirely fulfil the criteria described above. Some have a size over 100
81 nm, and cannot really be classify as nanoparticles according to international [15] and national
82 [16] organisations. Even if not everyone agrees on the 100 nm limit, sub-micron particles
83 would be a more appropriate denomination for particles of a size above 200 nm. A similar
84 comment can be made for nano-sized powder obtained after solvent evaporation. It is not

85 obvious that these nanoparticles are not agglomerated into larger clusters once dried. In that
86 case, properties arising from the nanometric-size such as luminescence may be retained, but
87 detection with a high resolution related with nanometric material will be lost. Moreover,
88 among nanoparticles used up-to-now few possess intrinsic luminescent properties. Most
89 metallic and metal-oxide nanoparticles present weak if no luminescence at all, restricting
90 their applications to light-coloured substrates only. Some attempts have been made to confer
91 luminescent properties to those nanoparticles types. For example, zinc oxide layer can be
92 added around gold nanoparticles to get luminescent fingerprint [17]. However, this
93 application remains limited to non-porous substrates and implies a tedious protocol. Another
94 option is to coat nanoparticles with a luminescent dye [8, 9, 18]. Among intrinsic luminescent
95 nanoparticles, quantum dots are the most commonly cited. These semi-conductor
96 nanoparticles are luminescent under UV excitation with a narrow emission peak. Their
97 emission colour is directly related to the size of the particles. This particular property is due
98 to quantum confinement effect [19, 20] and has driven a lot of endeavour towards their use as
99 a new tool for fingerprint detection [21-25, 26]. However, despite all efforts, few
100 publications present clear supporting evidence of their superiority over standard and
101 commonly used techniques. Cost, toxicity and tedious synthetic procedures set aside, the
102 main problem with quantum dots is the difficulty to properly functionalise their surface
103 without altering the structural properties and compromising the luminescence properties.
104 Very few occurrences of successfully and specifically functionalised particles for fingerprint
105 detection can be found. Some quantum dots have been functionalised with carboxyl or amine
106 groups [27], but despite the presented results, the real effect of the surface modification on
107 the detection properties remains unclear. This emphasises the fact that even if particles are
108 nano-sized and possess interesting optical properties, their surface still has to offer extensive
109 functionalisation properties in order to be successfully used for fingerprint detection.
110 Hence, despite all the nanoparticle types applied for fingerprint detection so far, none of
111 them really benefit at the same time from the three advantages presented above (i.e. small
112 size, optical properties and surface modifications). One kind of nanoparticles – yet
113 underrepresented in the literature – could regroup all the properties in one single entity: the
114 silicon oxide nanoparticles (SiO_2). This paper focuses on them and explores how they can
115 offer potential as a method for fingerprint detection. Silicon oxide nanoparticles consist of a
116 porous matrix of siloxane bonds, with an external layer of silanol groups that can further react
117 through hydrolysis and condensation with various alkoxysilanes, leading to a functionalised
118 layer covalently bound to the main matrix. As a consequence, SiO_2 nanoparticles could

119 present an almost unlimited range of functional groups. Dye molecules can be entrapped
120 within the siloxane matrix during the synthesis, providing a wide range of optical properties.
121 Various synthetic procedures exist, but two of them are most commonly considered: the
122 Stöber's synthesis and the reversed micro-emulsion. The Stöber's synthesis [28] leads to bulk
123 production, but the size and surface controls are limited. On the other end, reversed micro-
124 emulsion [29] enables to accurately control size, optical properties and functionalisation all at
125 the same time, but with a lower yield.

126 SiO₂ nanoparticles have been studied and successfully applied for fingerprint detection on
127 very rare occasions and with focus mostly put towards optical properties. Theaker et al.
128 investigated the use of hydrophobic micro- and nanoparticles containing sub-particles as well
129 as rhodamine 6G among other dyes [30]. Applied as a dried powder or in suspension, these
130 particles were shown to detect fingerprints on several non-porous substrates such as glass or
131 stainless steel. Finely grounded xerogel was synthesised using either a europium complex
132 [31] or rhodamine B [32]. Each of these dyes was used as powder dusting to detect marks.
133 More recently, 700 nm amphiphilic SiO₂ particles were applied on fingerprints on glass
134 microscopic slides but without any particular dyes embedded in their matrix [33].

135 In a recent study SiO₂ nanoparticles functionalised with various chemical groups and
136 dispersed in aqueous solutions were used to specifically study the interaction occurring
137 between fingerprint residues and nanoparticles [34]. It was demonstrated that chemical
138 interaction between carboxyl and amine groups could be promoted following three different
139 procedures: by lowering the pH of the solution, by adding sodium chloride (NaCl) to
140 decrease zeta potential intensity of the nanoparticles or by adding a diimide compound that
141 activates the amide linkage formation.

142
143 The study was focused on understanding the mechanism involved during the detection rather
144 than on the quality of the resulting detected mark. We think that gaining a better
145 understanding of the mechanism is a prerequisite to any work towards optimising the method.
146 This present study aims at exploring the possibilities offered by SiO₂ nanoparticles in terms
147 of a new tool for fingerprint detection, by optimising and comparing various detection
148 conditions, outer functionalisations and luminescent dyes. More work still needs to be
149 undertaken in order to provide a new fully operational technique, but the results obtained
150 during this study showed that SiO₂ nanoparticles are very promising and that research effort
151 should be further pursued.

152

153 **2. Materials and methods**

154 2.1 Synthesis and functionalisation of SiO₂ nanoparticles

155 SiO₂ nanoparticles were synthesised via reversed micro-emulsion where droplets of water
156 containing dye act as microreactors, allowing nanoparticles growth. Even if this method is
157 not the most cost-effective and has a low yield, it allowed synthesising nanoparticles with an
158 acute size control, introducing a dye in the matrix and functionalising nanoparticles surface,
159 all in a single synthetic process. Once nanoparticles were synthesised and functionalised, they
160 were precipitated out of the emulsion, washed and dissolved in water.

161 The same synthetic procedure described in Moret et al. was followed without any
162 modification [34]. Tetraethyl orthosilicate (TEOS), Triton X-100 (TX-100), cyclohexane, n-
163 hexanol, ammonium hydroxide (25 wt %), rhodamine 6G, rhodamine B, tris(2,2'-
164 bipyridyl)dichlororuthenium (II) hexahydrate (RuBpy) and sodium chloride (NaCl) were
165 purchased from Sigma-Aldrich. Carboxyethylsilanetriol sodium salt (CES) and 3-
166 (triethoxysilyl)-propylsuccinic anhydride (TES-PSA) were purchased from Abcr GmbH &
167 Co. All chemicals were used as received without further purification and were stable for
168 several months under storage conditions recommended by manufacturer. Briefly, the
169 synthetic procedure consisted in mixing 3.54 mL of TX-100, 15 mL of cyclohexane and 3.6
170 mL n-hexanol in a round bottom flask. 960 µL of a water-based dye solution were then
171 added. Three luminescent dyes (rhodamine 6G, rhodamine B and RuBpy) were tested in
172 order to compare optical properties. The dye concentration of the solution added during the
173 syntheses was 100 mM for both rhodamine 6G and rhodamine B, but for stability reasons it
174 was lowered to 16.6 mM for RuBpy, as recommended by Bagwe et al. [35]. After
175 stabilisation of the micro-emulsion, 200 µL of tetraethyl orthosilicate and 120 µL of
176 ammonium hydroxide were successively added to initiate nanoparticles formation. The
177 mixture was then kept under stirring for 24 h.

178 For the functionalisation step, two different silane coupling agents were used for comparison
179 purposed, CES and TES-PSA (Table 1), both containing carboxyl groups. This step was
180 conducted directly in the micro-emulsion mixture by adding 50 µL of tetraethyl orthosilicate
181 along with 170 µmol of either CES or TES-PSA. After 24 h, ethanol was added in large
182 excess in order to destabilise the emulsion. The precipitated solution was then centrifuged
183 and the functionalised nanoparticles were washed twice with ethanol and redispersed in 20
184 mL of RO/DI water.

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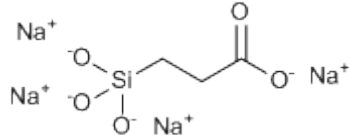
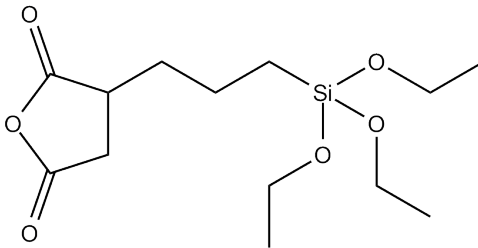
Name	Abbreviation	Molecular structure
carboxyethylsilanetriol sodium salt	CES	
3-(triethoxysilyl)-propylsuccinic anhydride	TES-PSA	

Table 1: Description of the two silane coupling agents used throughout the study.

187
188

189 2.2 Characterisation of the nanoparticles

190 Hydrodynamic diameters and zeta potentials of the synthesized SiO₂ nanoparticles were
191 respectively measured by dynamic light scattering and laser Doppler micro-electrophoresis
192 using a Zetasizer Nano ZS (Malvern Instrument Ltd). The procedure described in Moret et al.
193 was followed (i.e. hydrodynamic diameter was measured five times and zeta potential was
194 measure three time for each samples) [34].

195 An Hitachi F-2500 fluorescence spectrophotometer was used to measure photoluminescence
196 properties of the nanoparticles in solution. All measurements were performed at room
197 temperature on samples obtained after redispersing the nanoparticles in water.

198

199 2.3 Fingerprint sampling

200 In order to obtain realistic results, and as recommended in the guidelines published by the
201 International Fingerprint Research Group [36], only natural marks were collected. These
202 marks are said to be natural since no enrichment was made on purpose. The only restriction
203 was that the donors did not wash their hands half an hour prior deposition, but were asked to
204 behave normally otherwise. Three donors (one female, two males) were asked to deposit
205 series of marks on four different non-porous substrates (aluminium foils, black polyethylene
206 (PP), transparent polypropylene (PE) and glass). For the optimisation step, single appositions
207 were collected from one donor on aluminium foils. For the comparison step, sets of 20
208 successive depletive marks were collected for each donor and substrates. The samples were
209 left to age for one week, in an office drawer without specifically controlling the storage
210 conditions. To further test the technique, older marks on aluminium foils, transparent PP and
211 PE were processes as well (aged respectively of 18 months, 2 and 7 years). These marks

212 came from previous researches for which donors' identity, deposition and storage conditions
213 were unknown.

214

215 2.4 Fingerprint detection

216 Various parameters were successively assessed during this study. Three detection conditions
217 were evaluated and compared, as well as two functional groups containing carboxyl functions
218 and three luminescent dyes (Table 2).

219 Regardless of the chosen parameters, the overall detection protocol consists in a two-step
220 immersion procedure. The items are first immersed in a bath containing the nanoparticles
221 solution for 60 min (first two detection condition) or 30 min (third detection condition), then
222 rinsed with water. The rinsing step is necessary to remove any unwanted nanoparticles
223 remaining on the substrate, which could lead to background noise. Samples are then left to
224 air-dry.

225

226

Successive optimisations	Tested parameter		
	1. Detection conditions	pH 3 immersed 60 min	pH 6 NaCl 0.5 M immersed 60 min
2. Functionalisation	CES		TES-PSA
3. Luminescent dye	rhodamine 6G	rhodamine B	RuBpy

227

228 Table 2: Summary of the tested detection conditions and silicon oxide nanoparticles
229 properties.

230

231 2.5 Results comparison and evaluation

232 In order to determine if research on SiO₂ nanoparticles application was worth pursuing, the
233 results were compared to a commonly used technique: a one-step luminescent cyanoacrylate
234 the LumicyanoTM [37]. Each fingerprint was cut in half, one half being processed with the
235 nanoparticles solution and the other half fumed with LumicyanoTM (following the
236 manufacturer's instructions). For each fuming cycle, 1 g of LumicyanoTM was placed in
237 MVC1000 fuming cabinet (Foster & Freeman), at 80% of relative humidity. The samples
238 were exposed to cyanoacrylate fumes until the detection was considered as optimal (about 15
239 minutes). Since cyanoacrylate fuming results are generally dependent of the substrate type,
240 each surface was processed in a separate cycle.

241 Corresponding halves were then paired again before being photographed in luminescence
242 mode (Note: the luminescence of LumicyanoTM decreasing with time, the pictures were taken

243 the day of the fuming process). The imaging conditions were identical for LumicyanoTM and
244 SiO₂ nanoparticles, with an excitation at 495 nm (Minicrimescope MCS400) and an
245 observation at 590 nm (interferential filter with a band pass of 37 nm).

246 Results were assessed following the procedure described by Moret and Bécue [5]. Three
247 independent evaluators were presented one half mark at a time, in a random order. Each half
248 mark was thus assessed independently from its corresponding half. The average scores
249 obtained from each technique and substrate were then compared.

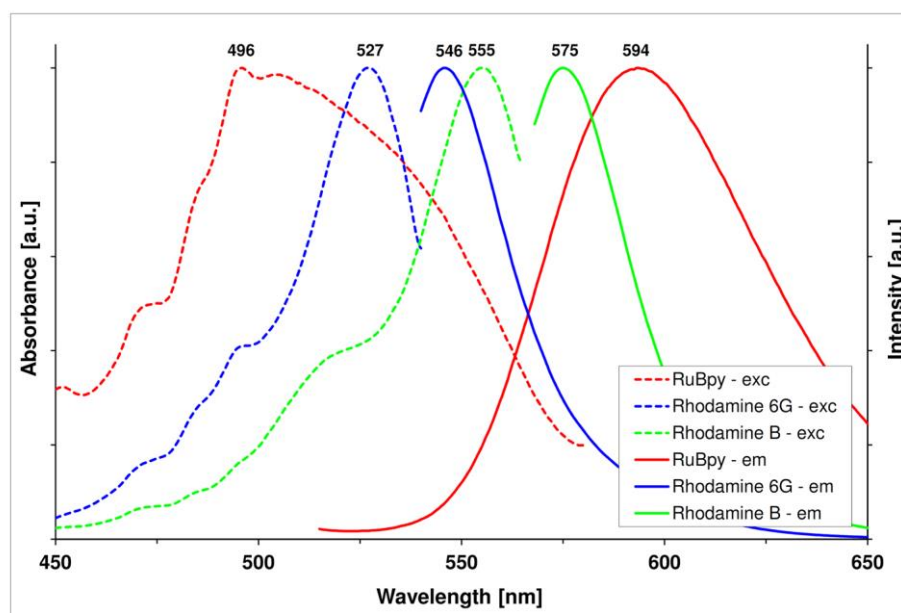
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251 3. Results and discussion

252 3.1 SiO₂ nanoparticles synthesis and characterisation

253 Nanoparticles solutions obtained via micro-emulsion were stable for months when stored at 4
254 °C in a fridge. DLS measurements gave an average hydrodynamic diameter of 84.2 nm and a
255 zeta potential of -36.7 mV at pH 6. These values were consistent with those obtained
256 previously [34].

257 Inclusion of dye molecules within the nanoparticles matrix helped obtaining various optical
258 properties (Figure 1). Rhodamine 6G, rhodamine B and RuBpy were selected because they
259 covered three distinct areas of the spectrum. They also have been used in previous studies
260 [30-32].



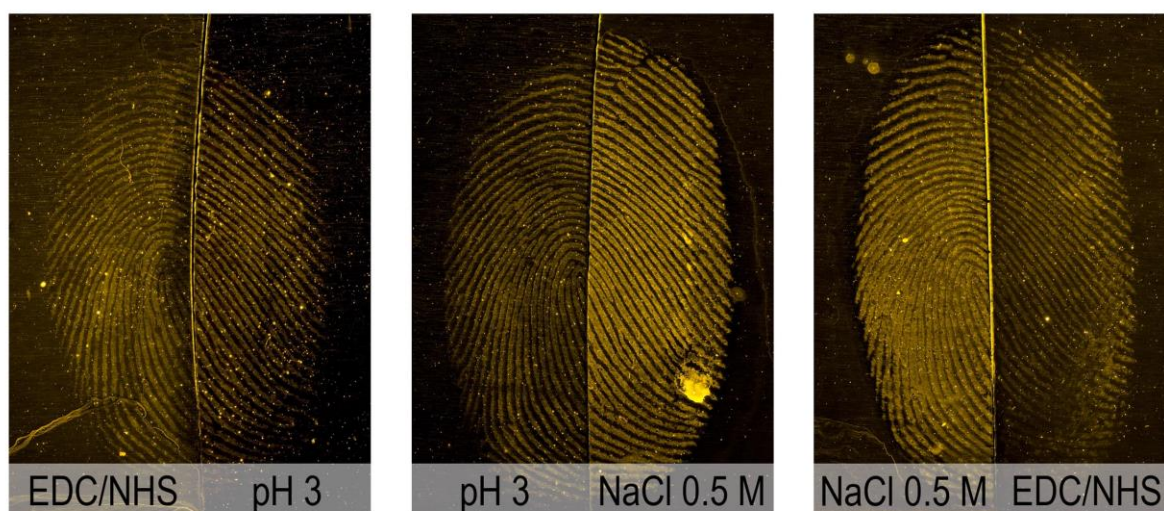
261

262 Figure 1: Excitation and emission spectra of silicon oxide nanoparticles solutions synthesised
263 with three different luminescent dyes (RuBpy, rhodamine 6G and rhodamine B)

264

265 3.2 Detection mode

266 Several parameters were compared to obtain better detection results. Three application modes
267 were previously determined to detect mark with success: adjusting the pH of the
268 nanoparticles solution to 3, adding sodium chloride (NaCl) to lower the zeta potential
269 intensity and adding a diimide compound to activate the carboxyl groups and favour the
270 interaction with the amine groups of the secretions [34].
271 These three detection modes were compared using the same nanoparticles batch containing
272 rhodamine 6G and functionalised with CES on fingerprints deposited on aluminium foils
273 (Figure 2). Luminescent results were successfully obtained in each case. It appeared however
274 that the best results in terms of ridge clarity and luminescence intensity were obtained when
275 NaCl was added in the solution to a concentration of 0.5 M. pH reduction and diimide
276 addition (EDC/NHS) led to slightly inferior results. Addition of NaCl was consequently
277 chosen as the best detection protocol and considered for the rest of the study.
278



279
280 Figure 2: Comparison between three application modes of Rhodamine 6G-doped SiO₂
281 nanoparticles solution (adding EDC/NHS, lowering the pH to 3 and adding NaCl to a
282 concentration of 0.5 M). Marks are one-week old, deposited on aluminium foil and visualised
283 in luminescent mode (excitation at 495 nm and emission at 590 nm).
284

285 3.3 Surface functionalisation

286 The second optimisation consisted in selecting the most appropriate function containing
287 carboxyl group that can interact with fingerprint residue. Two alkoxy silanes were grafted on
288 the surface of nanoparticles: CES and TES-PSA (Table 1). They both contain carboxyl group,
289 but the second one doubles the amount of functional groups present on the nanoparticle
290 surface, due to the opening of the succinic chain in water. Since carboxyl groups drive the
291 nanoparticles interaction with secretions, TES-PSA could lead to a better detection due to the

292 larger amount of reactive groups. Comparisons were made between two solutions containing
293 nanoparticles functionalised respectively with CES and TES-PSA. As determined previously,
294 NaCl (0.5 M) was added to favour the interaction. A significantly higher background noise
295 appeared with TES-PSA functionalised nanoparticles and the obtained marks appeared
296 blurred (Figure 3). With CES, an obvious quality difference was observed. Sharp luminescent
297 ridges were obtained, with clear level 3 features. Since CES functionalised nanoparticles gave
298 the best results, they were selected for this study.

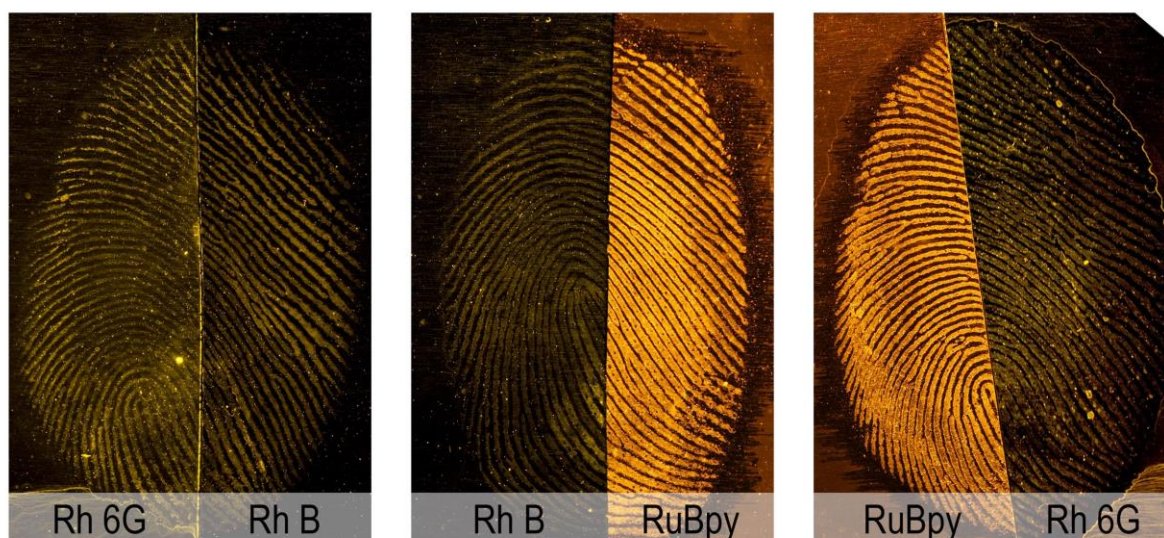


299
300 Figure 3: Comparison between Rhodamine 6G-doped silicon oxide nanoparticles
301 functionalised with TES-PSA ((triethoxysilyl)-propylsuccinic anhydride – left half) and CES
302 (carboxyethylsilanetriol – right half), and used to detect fingerprints. The illustrated
303 fingerprint is one-week old, deposited on aluminium foil and visualised in luminescent mode
304 (excitation at 495 nm and emission at 590 nm).
305

306 307 3.4 Luminescence properties

308 The last optimisation step was about the nanoparticles' optical properties. As described
309 above, three dyes were considered: rhodamine 6G used as a reference, rhodamine B and
310 RuBpy. Each half mark was observed under the luminescent conditions that lead to the best
311 result. RuBpy was illuminated at 495 nm, whereas both rhodamine 6G and rhodamine B were
312 excited at 515 nm. All marks were observed at 590 nm. These conditions differed from the
313 optimal conditions determined by spectrofluorimetry. If the theoretical conditions were to be
314 respected, the small Stokes shift of rhodamine 6G and B would lead to a background noise
315 due to the excitation wavelength. Based on the spectrofluorometry results (Figure 1), RuBpy
316 appeared to be the best choice since it has the larger Stokes shift (100 nm) compared to the
317 other two dyes (~20nm). These conditions were the one resulting in the best luminescence
318 intensity with the lowest background. Rhodamine 6G and rhodamine B showed equivalent

319 results in terms of luminescence intensity (Figure 4). RuBpy presented a much more intense
320 luminescence, compared to the two other dyes. It led to a light background staining, but since
321 RuBpy had a larger Stokes shift and the intensity of the final results was stronger, it was
322 chosen as the most suitable dye for this study. The observed background noise obtained after
323 immersing the samples was not judged detrimental to fingerprint visualisation.
324



325
326 Figure 4: Comparison between SiO₂ nanoparticles synthesised with three different
327 luminescent dyes (rhodamine 6G, rhodamine B and RuBpy). Marks are one-week old,
328 deposited on aluminium foil and visualised in luminescent mode (excitation at 495 nm and
329 emission at 590 nm).
330

331 These optimisation experiments led to select the parameters leading to the best detection
332 quality. Optimal detection was thus obtained with silicon oxide nanoparticles containing
333 RuBpy, functionalised with CES and applied in a solution at pH 6 containing 0.5 M of
334 sodium chloride for 60 min. Should this technique be applied on a larger scale, further
335 improvement would be needed, in order to reduce the immersion time for example. However,
336 results obtained so far constitute a valid base to conduct a comparison with a benchmark
337 technique.

338

339 3.5 Comparison with cyanoacrylate fuming

340 Conventional cyanoacrylate fuming is one of the most commonly used techniques for the
341 detection of fingerprints on non-porous substrates. However, it cannot be directly compared
342 to SiO₂ nanoparticles since the obtained results are not luminescent. In order to avoid
343 overestimating results and introducing a bias toward one technique or the other, a

344 luminescent technique should therefore be used to offer a valid comparison. Luminescent
345 marks can be obtained using conventional cyanoacrylate by following a two-step procedure
346 consisting in fumigating the samples first, then dye-staining them with a luminescent dye
347 dissolved in a solvent [38]. However, to avoid tedious staining procedures and to obtain more
348 homogeneous results throughout the sample sets, a one-step luminescent cyanoacrylate was
349 privileged during this study: the LumicyanoTM [37]. The obtained marks offer luminescent
350 properties either under UV (326 nm) or at 511 nm and the results can be observed with an
351 emission band centred at 562 nm. It however appeared that good luminescent marks could be
352 observed under the same conditions used for RuBpy (i.e. excitation at 495 nm and emission
353 filter at 590 nm). Using the same visualisation conditions help to image both sides at the
354 same time and to keep constant parameters for comparison.

355 Both techniques were applied on sets of 20 depletive marks from 3 donors on 4 different
356 substrates (a total of 240 marks) as described in the materials and methods section. The
357 samples were processed and imaged the same day in order to avoid any age inconsistency, or
358 luminescence intensity loss. Both techniques have been applied according to the established
359 procedure and led to satisfactory results. Under white light, the results obtained with
360 LumicyanoTM were similar to those that can be obtained with common cyanoacrylate.

361 Before discussing the sensibility obtained on depletive marks, the results obtained on the first
362 finger apposition are presented (Figure 5). Since results quality is related to the nature of the
363 substrate, they will be described separately. Aluminium foil is generally considered as an
364 ideal surface allowing good results to be obtained. Luminescent results were obtained for
365 both techniques, with a stronger intensity for LumicyanoTM (Figure 5 – first column).
366 However, when ridge details were considered, it can be seen that cyanoacrylate-fumed marks
367 tended to give dotted marks with ridge-continuity disruption. This was especially the case for
368 donors A and B, but not for donor C for which very homogenous results were obtained. This
369 phenomenon was however not observed for the fingermarks detected by SiO₂ nanoparticles.
370 Even if marks from donor B were not fully detected, nanoparticles developed marks with a
371 higher homogeneity for the three donors. An affinity of nanoparticles for the aluminium foil
372 was observed, leading to a slight background staining. This phenomenon, already noticed
373 during the optimisation phase, did not prevent fingermarks observation. The background was
374 not due to a lack of rinsing since it appears uniformly on the entire surface. It is most likely
375 due to unwanted interactions with the substrate. This issue could potentially be reduced by a
376 shorter immersion time in the nanoparticles solutions, and should be further studied. By
377 comparison, no background apparition was noticed with cyanoacrylate fuming.

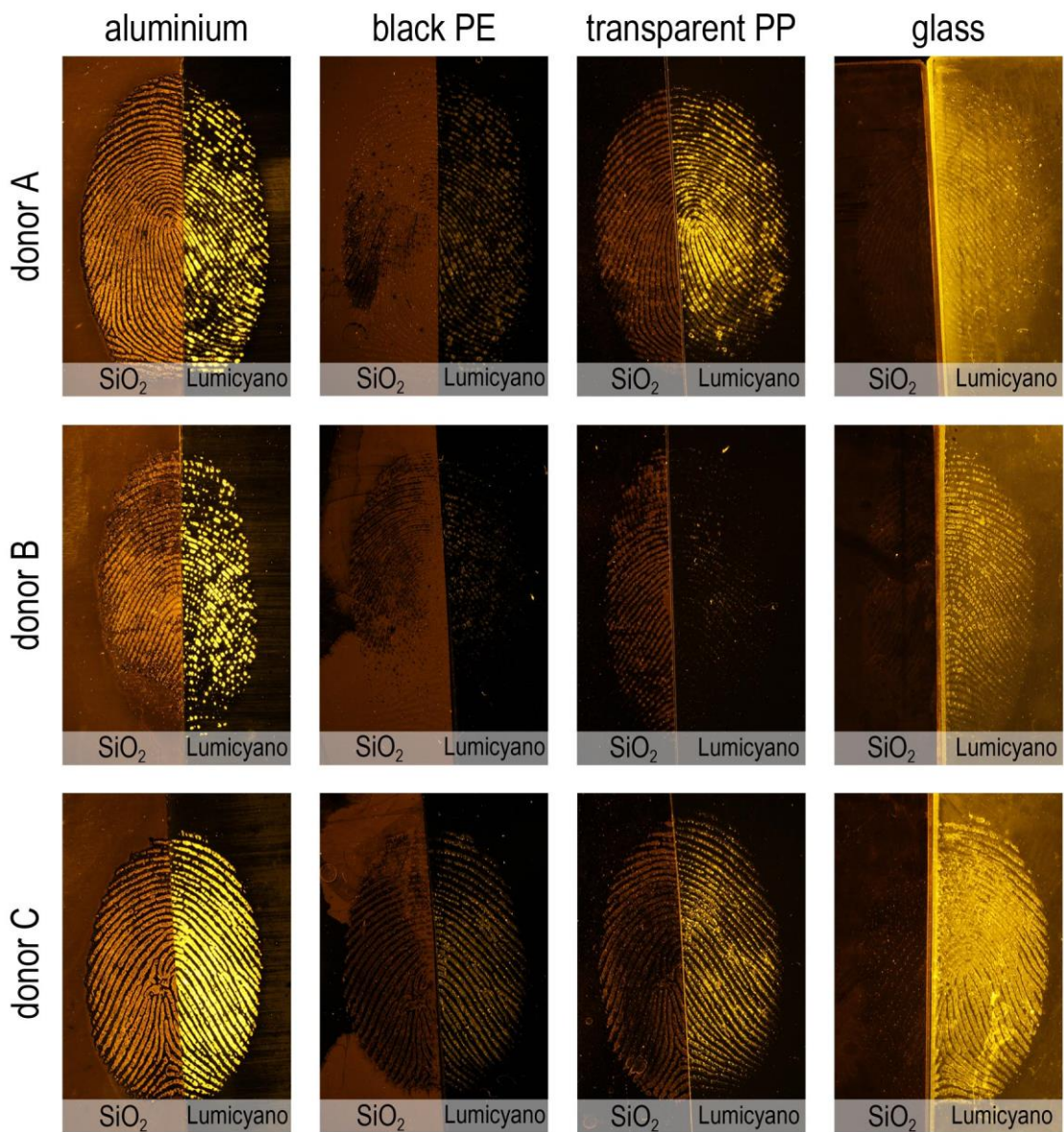
378 Regarding black PE, the previous observations were still valid (Figure 5 – second column).
379 Cyanoacrylate luminescence was less intense and led again to dotted marks. For donor B, the
380 marks were barely visible. The background noise observed with SiO₂ on aluminium foil is
381 much more pronounced on PE. Sometimes it concealed the marks almost entirely (donors A
382 and B). It was however not homogeneous and when absent it became possible to observe
383 luminescent marks of high quality with clear level 3 features (donor C). Nanoparticles were
384 thus effectively attracted on the secretions, but the ridges were partially covered by a non-
385 selective deposition onto the surface. That reinforces the needs of further studies on the
386 interaction with substrates.

387 Transparent PP provided significantly different results compared to the two previous
388 substrates (Figure 5 – third column). For the cyanoacrylate, luminescent marks were obtained
389 for both donor A and C, but the detection was not homogeneous towards the edge of the
390 donor A's mark and almost no ridges were visible for the donor B. The situation was quite
391 different for the SiO₂ nanoparticles; the detection itself was very homogeneous for all three
392 donors in terms of mark quality, with no background staining observed. .

393 On glass, the nanoparticles solution has largely washed away the marks (Figure 5 – second
394 last). Only a weak luminescence and low quality marks were observed. On the other halves,
395 cyanoacrylate performed well for the three donors, even if a light background staining
396 appeared. Considering SiO₂ nanoparticles, the detection protocol seems not appropriate for
397 this type of substrate and should thus be further adjusted. Reduction of immersion time or
398 finding another carrier solvent could be key factors that could lead to better results.

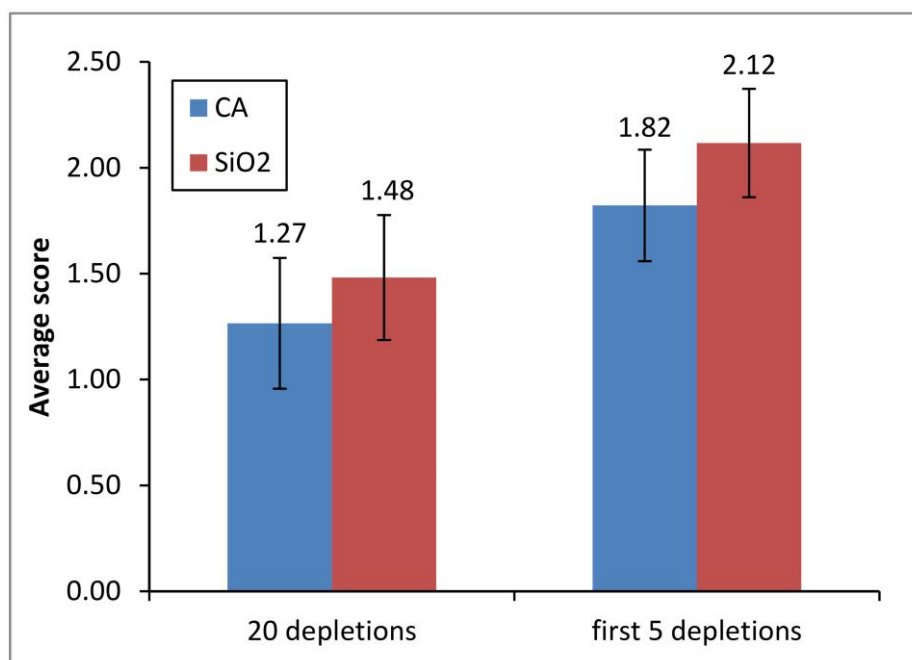
399 In summary, for the first marks of the depletion series, cyanoacrylate succeeded in detecting
400 marks on all tested surfaces. However, differences in quality were consistently observed
401 between donors. These variations can be attributed to the quantity and quality variation
402 among donors' secretions. However, this trend was less pronounced with SiO₂ nanoparticles
403 that react not with specific compounds of the secretion, but with specific functional groups.
404 The results quality was however more tightly related to the substrate type, which indicates
405 that the detection conditions can be further adjusted. Glass appeared to be a challenging
406 surface since nanoparticles solution tended to wash the secretion, and thus failing in detecting
407 any mark. Moreover, background staining appeared on black PE, impinging the detection of
408 the marks. Future optimisations need to be carried on, especially to decrease the unwanted
409 background staining and to obtain a more versatile technique that could be applied on a wider
410 range of substrates. SiO₂ nanoparticles application remains promising since the obtained

411 results are very homogeneous and appeared to be less donor-dependent. This, in itself,
412 represents a considerable advantage over cyanoacrylate fuming.
413



414
415 Figure 5: Comparison of fingerprints detected with RuBpy-doped silicon oxide nanoparticles
416 (left halves) and LumicyanoTM (right halves) from three donors on four substrates.
417

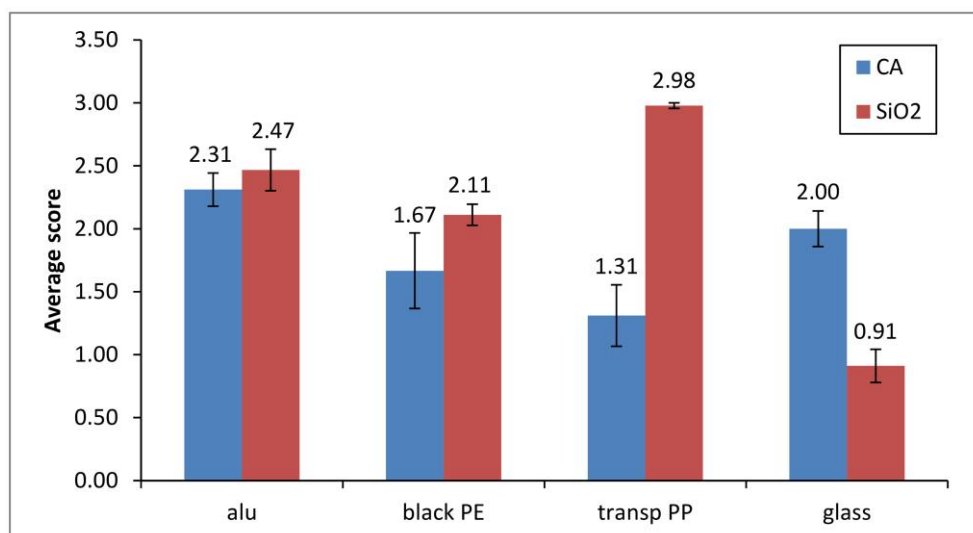
418 Results obtained with the depletive series are presented below. On average, by taking into
419 account every mark from each donor and substrate, comparable scores were obtained for both
420 techniques (1.3 for LumicyanoTM and 1.5 for SiO₂ nanoparticles) (Figure 6). When only the
421 first five depletions were considered, a general increase of scores was noticed (1.8 for
422 LumicyanoTM and 2.1 for SiO₂ nanoparticles), showing that nanoparticles gave slightly better
423 results on average (Figure 6).



425

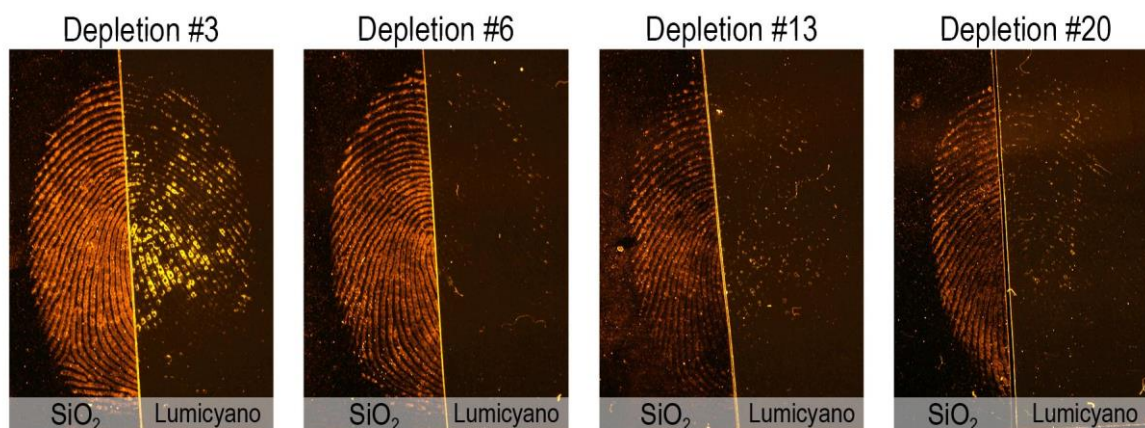
426 Figure 6: Comparison of the average results obtained with LumicyanoTM (CA) and RuBpy-
427 doped SiO₂ nanoparticles.
428

429 By looking at each substrate separately and considering only the first five depletions, results
430 can be described in more details (Figure 7). On aluminium foil, equivalent results were
431 obtained showing that both techniques performed well, but on glass, as described above, SiO₂
432 solution tends to wash the marks, leading to low quality results, cyanoacrylate fuming shows
433 superior scores. For the black PE, even if background staining was observed, the average
434 quality was still superior for SiO₂ nanoparticles compared to cyanoacrylate. The biggest
435 difference appeared on transparent PP where cyanoacrylate stopped being effective after just
436 a few depletions, while SiO₂ nanoparticles kept detecting marks. This was not only true for
437 the first five depletions, good quality results were obtained until the twentieth depletion
438 (Figure 8).



439

440 Figure 7: Comparison of the average results obtained with Lumicyano™ (CA) and RuBpy-
 441 doped SiO₂ nanoparticles on four different substrates.
 442

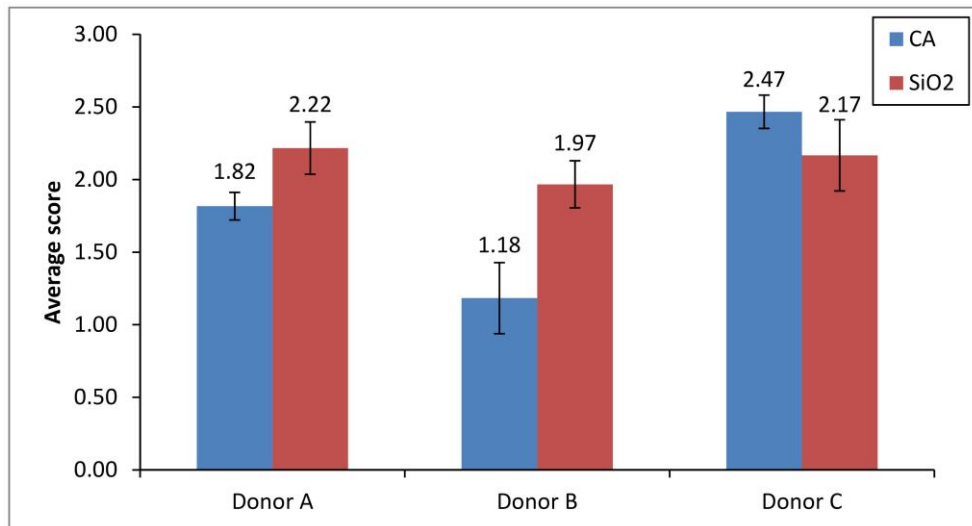


443

444 Figure 8: Comparison of depletive fingermarks detected with RuBpdy-doped silicon oxide
 445 nanoparticles (left halves) and luminescent cyanoacrylate (right halves) on transparent PP.
 446

447 When average scores were calculated considering each donor individually, SiO₂
 448 nanoparticles were less donor dependent than cyanoacrylate (Figure 9). The calculated
 449 variance between donors for cyanoacrylate is 0.41, whereas the one for SiO₂ nanoparticles is
 450 only 0.02.

451 To compare the efficiency of the two techniques over the entire depletion series, marks of a
 452 score above or equal to 2 were added (Figure 10). Cyanoacrylate on aluminium detected the
 453 greatest amount of marks. SiO₂ nanoparticles solution, as detailed above, was not efficient on
 454 glass, but detected a comparable amount of marks on the three other substrates.



455

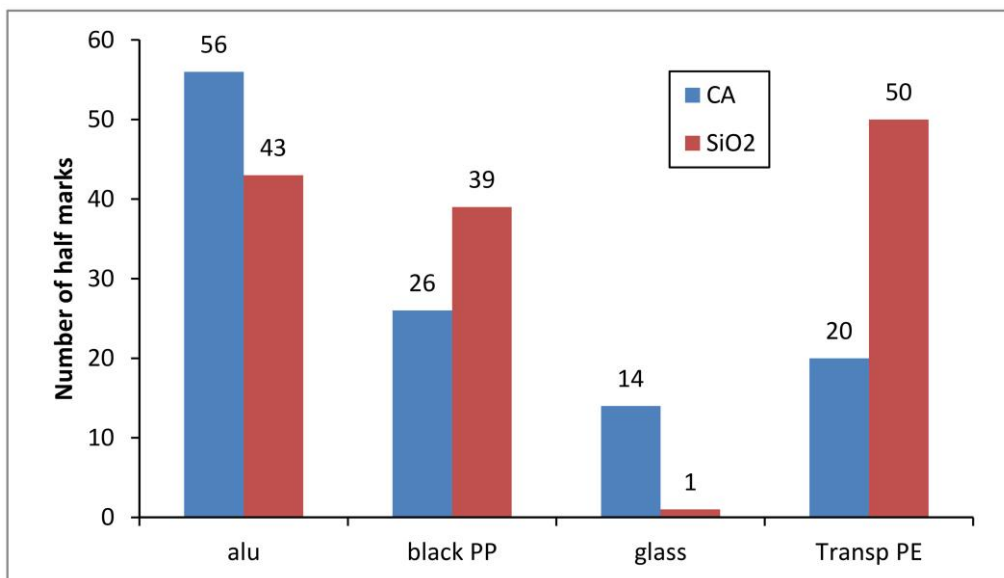
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Figure 9: Comparison of the average results obtained from three different donors with LumicyanoTM (CA) and RuBpy-doped SiO₂ nanoparticles.



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Figure 10: Comparison between the amount of mark with a score equal or above 2 detected per substrate for each technique.

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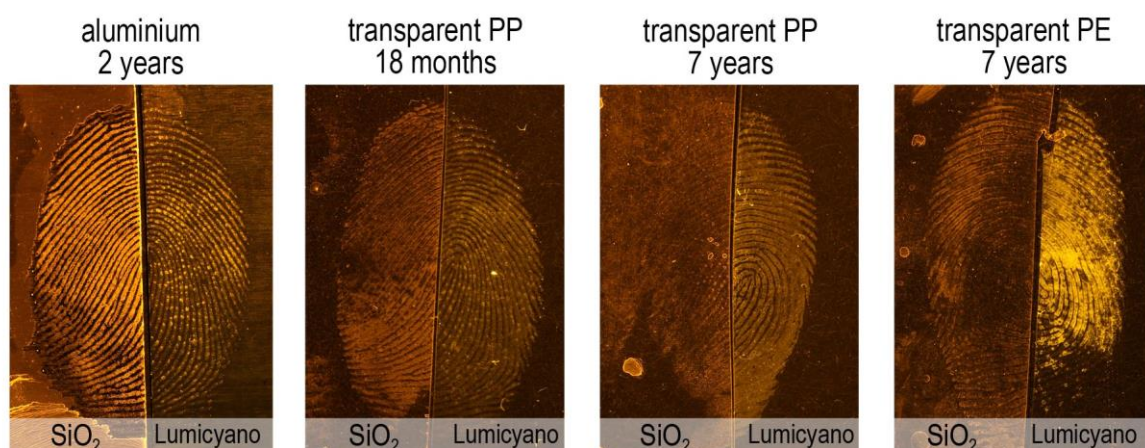
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To conclude the comparisons, aged marks on aluminium foils, transparent PP and PE were process following the same established protocol. Both cyanoacrylate fuming and SiO₂ nanoparticles solution were able to detect marks as old as 7 years. On aluminium foils, SiO₂ nanoparticles tended to give better ridge details. The reversed situation was observed on transparent PP. For the 7 years marks, LumicyanoTM was superior on transparent PP, with much better ridge quality. On PE, more completed marks were detected with SiO₂ nanoparticles, despite missing information in the centre, whereas cyanoacrylate presented good details on the upper part and very few details on the lower part.



473

474 Figure 11: Comparison of old fingerprints (18 months to 7 years) detected with RuBpy-
 475 doped silicon oxide nanoparticles (left halves) and LumicyanoTM (right halves) on three
 476 substrates.
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479

4. Conclusions

480 This paper investigated an application of luminescent functionalised SiO₂ nanoparticles for
 481 fingerprint detection. Several optimisations of the detection protocol for considering dye-
 482 doped SiO₂ nanoparticles as efficient fingerprint reagents were presented. Appropriate
 483 detection conditions, outer functionalisations and luminescent dyes were successively studied
 484 and selected, leading to an optimised protocol. A comparison to LumicyanoTM, a one-step
 485 luminescent cyanoacrylate (CA), was then conducted to assess the efficiency of the method.
 486 Both techniques were compared on series of 20 depletive marks from three donors on four
 487 different non-porous substrates.

488 On average, both techniques performed similarly. However, for LumicyanoTM, quality
 489 variations between donors were observed. Interestingly, that was not observed (or only to a
 490 limited extent) for SiO₂ nanoparticles. This might be due to the fact that the technique targets
 491 a specific functional group instead of particular compounds of the secretion. The SiO₂ results
 492 quality was instead more related to the substrate type.

493 Heterogeneous detection results proved that the technique remained to be further optimised.
 494 Regarding health and safety issue about SiO₂ nanoparticles application, no toxicity
 495 assessment of the synthesized nanoparticles was performed in this study. This should be
 496 considered in details before any large scale application. More work still needs to be
 497 undertaken in order to provide a fully operational technique, but the reported results in this

498 study showed that SiO₂ nanoparticles are very promising and that research effort should be
499 further pursued.

500

501

502 **References**

503 [1] Bécue A., Moret S., Champod C., Margot P. (2011), Use of stains to detect
504 fingerprints, *Biotechnic & Histochemistry*, **86**, 140-160.

505 [2] Chadwick S., Maynard P., Kirkbride P., Lennard C., Spindler X., Roux C. (2011), Use
506 of styryl 11 and STaR 11 for the luminescence enhancement of cyanoacrylate-
507 developed fingerprints in the visible and near-infrared regions, *Journal of Forensic*
508 *Sciences*, **56**, 1505-1513.

509 [3] Leggett R., Lee-Smith E. E., Jickells S. M., Russell D. A. (2007), "Intelligent"
510 fingerprinting: Simultaneous identification of drug metabolites and individuals by using
511 antibody-functionalized nanoparticles, *Angewandte Chemie International Edition*, **46**,
512 4100-4103.

513 [4] Schnetz B., Margot P. (2001), Technical note: Latent fingerprints, colloidal gold and
514 multimetal deposition (MMD) optimisation of the method, *Forensic Science*
515 *International*, **118**, 21-28.

516 [5] Moret S., Bécue A. (2015), Single-metal deposition for fingerprint detection—a
517 simpler and more efficient protocol, *Journal of Forensic Identification*, **65**, 118-137.

518 [6] Cantú A. A., Johnson J. L. (2001), Silver physical development of latent prints, In:
519 *Advances in fingerprint technology, 2nd ed.*, Lee, H. C., Gaensslen, R. E., Eds., CRC
520 Press: Boca Raton, FL; pp 241-274.

521 [7] Wade D. C. (2002), Development of latent prints with titanium dioxide (TiO₂), *Journal*
522 *of Forensic Identification*, **52**, 551-559.

523 [8] Sodhi G. S., Kaur J. (2006), Nanoparticle size fingerprint dusting composition based on
524 fluorescent eosin Y dye, *Fingerprint Whorld*, **32**, 146-147.

525 [9] Sodhi G. S., Kaur J. (2007), A novel, nanoparticle size fingerprint detecting
526 composition based on fluorescent lucifer Y stain, *Fingerprint Whorld*, **34**, 24-25.

527 [10] Choi M. J., McBean K. E., Ng P. H. R., McDonagh A. M., Maynard P. J., Lennard C.,
528 Roux C. (2008), An evaluation of nanostructured zinc oxide as a fluorescent powder for
529 fingerprint detection, *Journal of Materials Science*, **43**, 732-737.

530 [11] Bécue A., Moret S., Champod C., Margot P. (2009), Use of quantum dots in aqueous
531 solution to detect blood fingerprints on non-porous surfaces, *Forensic Science*
532 *International*, **191**, 36-41.

533 [12] Dilag J., Kobus H., Ellis A. V. (2009), Cadmium sulfide quantum dot/chitosan
534 nanocomposites for latent fingerprint detection, *Forensic Science International*, **187**,
535 97-102.

536 [13] Dilag J., Kobus H. J., Ellis A. V. (2011), Nanotechnology as a new tool for fingerprint
537 detection: A review, *Current Nanoscience*, **7**, 153-159.

538 [14] Bécue A., Cantú A. A. (2012), Fingerprint detection using nanoparticles, In: *Lee and*
539 *Gaensslen's advances in fingerprint technology, 3rd ed.*, Ramotowski, R. S., Ed., CRC
540 Press LLC; pp 307-379.

541 [15] ASTM International (2006), Standard terminology relating to nanotechnology; ASTM
542 International, Ed.; Vol. E 2456 - 06.

543 [16] British Standards Institution (2005), Vocabulary - nanoparticles; British Standards
544 Institution, Ed.; Vol. PAS 71:2005.

- 545 [17] Bécue A., Scoundrianos A., Champod C., Margot P. (2008), Fingermark detection
546 based on the in situ growth of luminescent nanoparticles - towards a new generation of
547 multimetal deposition, *Forensic Science International*, **179**, 39-43.
- 548 [18] Chadwick S., Maynard P., Kirkbride P., Lennard C., McDonagh A., Spindler X., Roux
549 C. (2012), Styryl dye coated metal oxide powders for the detection of latent
550 fingermarks on non-porous surfaces, *Forensic Science International*, **219**, 208-214.
- 551 [19] Alivisatos A. P. (1996), Semiconductor clusters, nanocrystals and quantum dots,
552 *Science*, **271**, 933-937.
- 553 [20] Bukowski T. J., Simmons J. H. (2002), Quantum dot research: Current state and future
554 prospects, *Critical Reviews in Solid State and Materials Sciences*, **27**, 119-142.
- 555 [21] Menzel R. E. (2000), Photoluminescence detection of latent fingerprints with quantum
556 dots for time-resolved imaging, *Fingerprint Whorld*, **26**, 119-123.
- 557 [22] Cheng K. H., Ajimo J., Chen W. (2008), Exploration of functionalized CdTe
558 nanoparticles for latent fingerprint detection, *Journal of Nanoscience and
559 Nanotechnology*, **8**, 1170-1173.
- 560 [23] Moret S., Bécue A., Champod C. (2013), Cadmium-free quantum dots in aqueous
561 solution: Potential for fingermark detection, synthesis and an application to the
562 detection of fingermarks in blood on non-porous surfaces, *Forensic Science
563 International*, **224**, 101-110.
- 564 [24] Yu X., Liu J., Zuo S., Yu Y., Cai K., Yang R. (2013), Application of mercaptosuccinic
565 acid capped CdTe quantum dots for latent fingermark development, *Forensic Science
566 International*, **231**, 125-130.
- 567 [25] Wang Y. F., Yang R. Q., Shi Z. X., Liu J. J., Zhao K., Wang Y. J. (2014), The
568 effectiveness of CdSe nanoparticle suspension for developing latent fingermarks,
569 *Journal of Saudi Chemical Society* **18**, 13-18.
- 570 [26] Xu C., Zhou R., He W., Wu L., Wu P., Hou X. (2014), Fast imaging of eccrine latent
571 fingerprints with nontoxic mn-doped ZnS QDs, *Analytical Chemistry*, **86**, 3279-3283.
- 572 [27] Gao F., Han J., Zhang J., Li Q., Sun X., Zheng J., Bao L., Li X., Liu Z. (2011), The
573 synthesis of newly modified CdTe quantum dots and their application for improvement
574 of latent fingerprint detection, *Nanotechnology*, **22**, art. No. 075705 (10 pp.).
- 575 [28] Stöber W., Fink A., Bohn E. (1968), Controlled growth of monodisperse silica spheres
576 in the micron size range, *Journal of Colloid and Interface Science*, **26**, 62-69.
- 577 [29] López-Quintela A. (2003), Synthesis of nanomaterials in microemulsions: Formation
578 mechanisms and growth control, *Current Opinion in Colloid and Interface Science*, **8**,
579 137-144.
- 580 [30] Theaker B. J., Hudson K. E., Rowell F. J. (2008), Doped hydrophobic silica nano- and
581 micro-particles as novel agents for developing latent fingerprints, *Forensic Science
582 International*, **174**, 26-34.
- 583 [31] Liu L., Gill S. K., Gao Y., Hope-Weeks L. J., Cheng K. H. (2008), Exploration of the
584 use of novel SiO₂ nanocomposites doped with fluorescent Eu³⁺/sensitizer complex for
585 latent fingerprint detection, *Forensic Science International*, **176**, 163-172.
- 586 [32] Liu L. (2011), Study on the use of rhodamine doped nanocomposite for latent
587 fingerprint detection, *Advanced Materials Research*, **295-297**, 813-816.
- 588 [33] Huang W., Li X., Wang H., Xu X., Liu H., Wang G. (in press), Synthesis of
589 amphiphilic silica nanoparticles for latent fingerprint detection, *Analytical Letters*.
- 590 [34] Moret S., Bécue A., Champod C. (2014), Nanoparticles for fingermark detection: An
591 insight into the reaction mechanism, *Nanotechnology*, **25**, 425502.
- 592 [35] Bagwe R. P., Yang C., Hilliard L. R., Tan W. (2004), Optimization of dye-doped silica
593 nanoparticles prepared using a reverse microemulsion method, *Langmuir*, **20**, 8336-
594 8342.

- 595 [36] International Fingerprint Research Group (IFRG) (2014), Guidelines for the assessment
596 of fingermark detection techniques, *Journal of Forensic Identification*, **64**, 174-200.
- 597 [37] Prete C., Galmiche L., Quenum-Possy-Berry F.-G., Allain C., Thiburce N., Colard T.
598 (2013), LumicyanoTM: A new fluorescent cyanoacrylate for a one-step luminescent
599 latent fingermark development, *Forensic Science International*, **233**, 104-112.
- 600 [38] Mazzella W. D., Lennard C. (1995), An additional study of cyanoacrylate stains,
601 *Journal of Forensic Identification*, **45**, 5-18.

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