

Proposition of: paper

Functionalised silicon oxide nanoparticles for fingerprint detection

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1 **Abstract:**

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

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

18

19 **Keywords:** Nanotechnology, luminescence, sensitivity, selectivity, cyanoacrylate, non-
20 porous substrates.

21

22 **1. Introduction**

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

38 Over the past decade, these advantages attracted a lot of attention and a substantial number of
39 nanoparticle types have been studied and applied with varying success. They can be sorted
40 into three categories, i.e. metal, metal oxide and semi-conductors. Gold and silver
41 nanoparticles have been successfully used in techniques such as multi- or single-metal
42 deposition (gold) [4, 5] or physical developer (silver) [6]. Among metal oxides, we can cite
43 titanium dioxide (TiO_2) [7], aluminium oxide (Al_2O_3) [8, 9] or zinc oxide (ZnO) [10]. Metal
44 oxides are generally applied as dried powders, sometimes functionalised with aliphatic chains
45 to increase and favour hydrophobic interactions with greasy components of the fingerprint
46 residue. Quantum dots are the most studied class of semiconductors. They attracted a lot of
47 attention mostly for their uncommon optical properties [11, 12]. This paper does not intend to
48 describe these nanoparticles in extensive details; thorough reviews are available elsewhere
49 [13, 14].

50 However, from a critical viewpoint, none of the nanoparticles studied until now and their
51 subsequent applications entirely fulfil the criteria described above. Some have a size over 100
52 nm, and cannot really be classify as nanoparticles according to international [15] and national
53 [16] organisations. Even if not everyone agrees on the 100 nm limit, sub-micron particles
54 would be a more appropriate denomination for particles of a size above 200 nm. A similar
55 comment can be made for nano-sized powder obtained after solvent evaporation. It is not

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

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

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

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

113
114 The study was focused on understanding the mechanism involved during the detection rather
115 than on the quality of the resulting detected mark. We think that gaining a better
116 understanding of the mechanism is a prerequisite to any work towards optimising the method.
117 This present study aims at exploring the possibilities offered by SiO₂ nanoparticles in terms
118 of a new tool for fingerprint detection, by optimising and comparing various detection
119 conditions, outer functionalisations and luminescent dyes. More work still needs to be
120 undertaken in order to provide a new fully operational technique, but the results obtained
121 during this study showed that SiO₂ nanoparticles are very promising and that research effort
122 should be further pursued.

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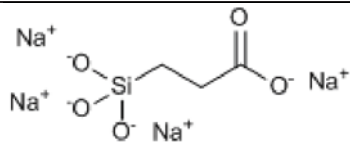
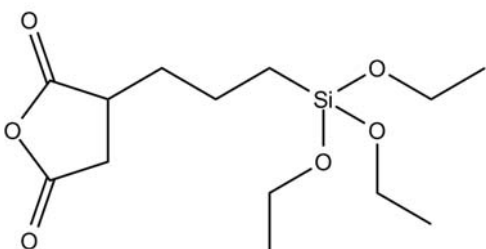
124 2. Materials and methods

125 2.1 Synthesis and functionalisation of SiO₂ nanoparticles

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

132 The same synthetic procedure described in Moret et al. was followed without any
133 modification [34]. Three luminescent dyes (rhodamine 6G, rhodamine B and tris(2,2'-
134 bipyridyl)dichlororuthenium (II) hexahydrate (RuBpy)) were tested in order to compare
135 optical properties. The dye concentration of the solution added during the syntheses was
136 100 mM for both rhodamine 6G and rhodamine B, but for stability reasons it was lowered to
137 16.6 mM for RuBpy, as recommended by Bagwe et al. [35]. For the functionalisation step,
138 two different silane coupling agents were used for comparison purposed (Table 1)
139 (carboxyethylsilanetriol sodium salt (CES) and 3-(triethoxysilyl)-propylsuccinic anhydride
140 (TES-PSA)). They both contained carboxyl groups.

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

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

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144 2.2 Characterisation of the nanoparticles

145 Hydrodynamic diameters and zeta potentials of the synthesized SiO₂ nanoparticles were
146 respectively measured by dynamic light scattering and laser Doppler micro-electrophoresis
147 using a Zetasizer Nano ZS (Malvern Instrument Ltd). The procedure described in Moret et al.

148 was followed (i.e. hydrodynamic diameter was measured five times and zeta potential was
149 measure three time for each samples) [34].

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

153

154 2.3 Fingermark sampling

155 In order to obtain realistic results, and as recommended in the guidelines published by the
156 International Fingerprint Research Group [36], only natural marks were collected. These
157 marks are said to be natural since no enrichment was made on purpose. The only restriction
158 was that the donors did not wash their hands half an hour prior deposition, but were asked to
159 behave normally otherwise. Three donors (one female, two males) were asked to deposit
160 series of marks on four different non-porous substrates (aluminium foils, black polyethylene
161 (PP), transparent polypropylene (PE) and glass). For the optimisation step, single appositions
162 were collected from one donor on aluminium foils. For the comparison step, sets of 20
163 successive depletive marks were collected for each donor and substrates. The samples were
164 left to age for one week, in an office drawer without specifically controlling the storage
165 conditions. To further test the technique, older marks on aluminium foils, transparent PP and
166 PE were processes as well (aged respectively of 18 months, 2 and 7 years). These marks
167 came from previous researches for which donors' identity, deposition and storage conditions
168 were unknown.

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170 2.4 Fingermark detection

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

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

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Successive optimisations	Tested parameter		
1. Detection conditions	pH 3 immersed 60 min	pH 6 NaCl 0.5 M immersed 60 min	EDC/NHS immersed 30 min
2. Functionalisation	CES		TES-PSA
3. Luminescent dye	rhodamine 6G	rhodamine B	RuBpy

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

2.5 Results comparison and evaluation

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

Corresponding halves were then paired again before being photographed in luminescence mode (Note: the luminescence of LumicyanoTM decreasing with time, the pictures were taken the day of the fuming process). The imaging conditions were identical for LumicyanoTM and SiO₂ nanoparticles, with an excitation at 495 nm (Minicrimescope MCS400) and an observation at 590 nm (interferential filter with a band pass of 37 nm).

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

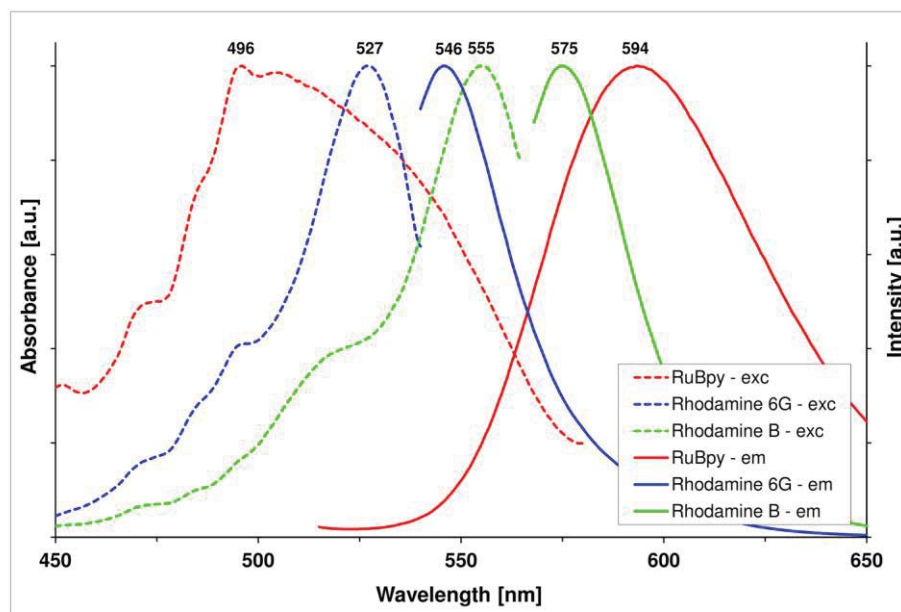
3. Results and discussion

3.1 SiO₂ nanoparticles synthesis and characterisation

Reversed micro-emulsion allowed obtaining stable solutions. DLS measurements gave an average hydrodynamic diameter of 84.2 nm and a zeta potential of -36.7 mV at pH 6. These values were consistent with those obtained previously [34].

Inclusion of dye molecules within the nanoparticles matrix helped obtaining various optical properties (Figure 1). Rhodamine 6G, rhodamine B and RuBpy were selected because they

213 covered three distinct areas of the spectrum. They also have been used in previous studies
214 [30-32].



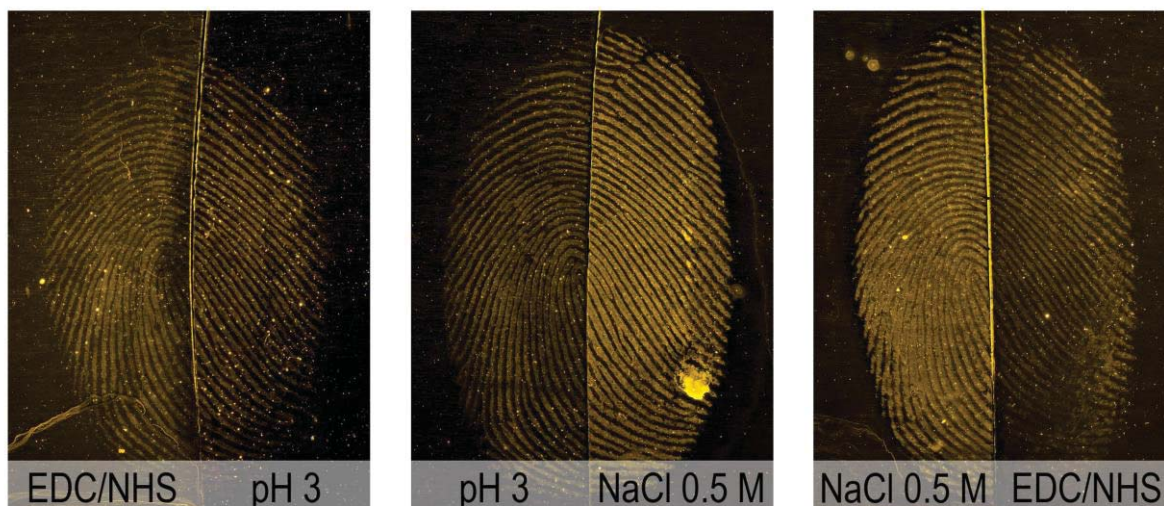
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216 Figure 1: Excitation and emission spectra of silicon oxide nanoparticles solutions synthesised
217 with three different luminescent dyes (RuBpy, rhodamine 6G and rhodamine B)
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219 3.2 Detection mode

220 Several parameters were compared to obtain better detection results. Three application modes
221 were previously determined to detect mark with success: adjusting the pH of the
222 nanoparticles solution to 3, adding sodium chloride (NaCl) to lower the zeta potential
223 intensity and adding a diimide compound to activate the carboxyl groups and favour the
224 interaction with the amine groups of the secretions [34].

225 These three detection modes were compared using the same nanoparticles batch containing
226 rhodamine 6G and functionalised with CES on fingerprints deposited on aluminium foils
227 (Figure 2). Luminescent results were successfully obtained in each case. It appeared however
228 that the best results in terms of ridge clarity and luminescence intensity were obtained when
229 NaCl was added in the solution to a concentration of 0.5 M. pH reduction and diimide
230 addition (EDC/NHS) led to slightly inferior results. Addition of NaCl was consequently
231 chosen as the best detection protocol and considered for the rest of the study.

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

239 3.3 Surface functionalisation

240 The second optimisation consisted in selecting the most appropriate function containing
241 carboxyl group that can interact with fingerprint residue. Two alkoxysilanes were grafted on
242 the surface of nanoparticles: CES and TES-PSA (Table 1). They both contain carboxyl group,
243 but the second one doubles the amount of functional groups present on the nanoparticle
244 surface, due to the opening of the succinic chain in water. Since carboxyl groups drive the
245 nanoparticles interaction with secretions, TES-PSA could lead to a better detection due to the
246 larger amount of reactive groups. Comparisons were made between two solutions containing
247 nanoparticles functionalised respectively with CES and TES-PSA. As determined previously,
248 NaCl (0.5 M) was added to favour the interaction. A significantly higher background noise
249 appeared with TES-PSA functionalised nanoparticles and the obtained marks appeared
250 blurred (Figure 3). With CES, an obvious quality difference was observed. Sharp luminescent
251 ridges were obtained, with clear level 3 features. Since CES functionalised nanoparticles gave
252 the best results, they were selected for this study.



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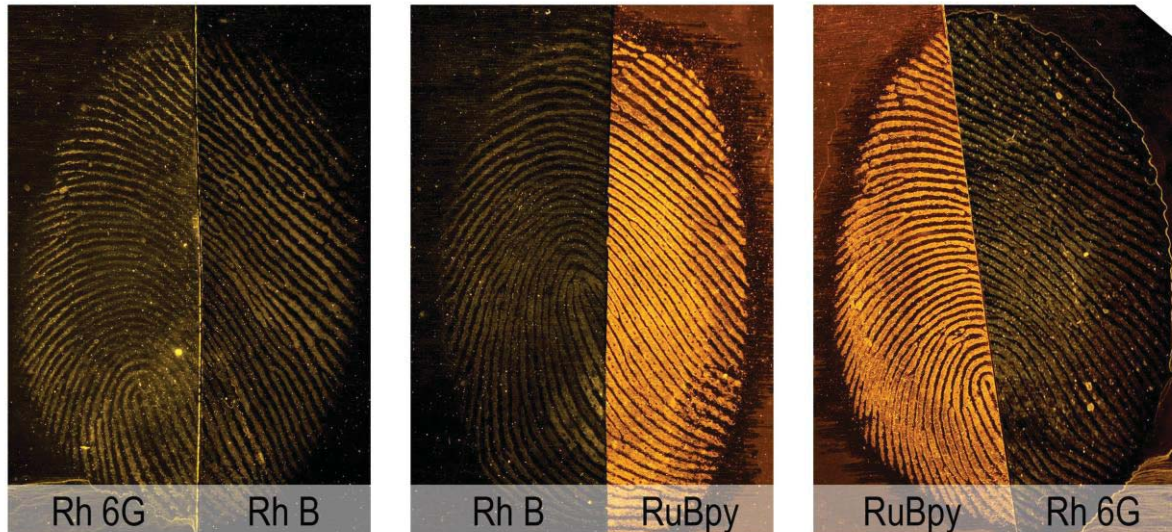
Figure 3: Comparison between Rhodamine 6G-doped silicon oxide nanoparticles functionalised with TES-PSA ((triethoxysilyl)-propylsuccinic anhydride – left half) and CES (carboxyethylsilanetriol – right half), and used to detect fingermarks. The illustrated fingerprint is one-week old, deposited on aluminium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

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261 3.4 Luminescence properties

262 The last optimisation step was about the nanoparticles' optical properties. As described
263 above, three dyes were considered: rhodamine 6G used as a reference, rhodamine B and
264 RuBpy. Each half mark was observed under the luminescent conditions that lead to the best
265 result. RuBpy was illuminated at 495 nm, whereas both rhodamine 6G and rhodamine B were
266 excited at 515 nm. All marks were observed at 590 nm. These conditions differed from the
267 optimal conditions determined by spectrofluorimetry. If the theoretical conditions were to be
268 respected, the small Stokes shift of rhodamine 6G and B would lead to a background noise
269 due to the excitation wavelength. Based on the spectrofluorometry results (Figure 1), RuBpy
270 appeared to be the best choice since it has the larger Stokes shift (100 nm) compared to the
271 other two dyes (~20nm). These conditions were the one resulting in the best luminescence
272 intensity with the lowest background. Rhodamine 6G and rhodamine B showed equivalent
273 results in terms of luminescence intensity (Figure 4). RuBpy presented a much more intense
274 luminescence, compared to the two other dyes. It led to a light background staining, but since
275 RuBpy had a larger Stokes shift and the intensity of the final results was stronger, it was
276 chosen as the most suitable dye for this study. The observed background noise obtained after
277 immersing the samples was not judged detrimental to fingerprint visualisation.

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

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

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3.5 Comparison with cyanoacrylate fuming

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Conventional cyanoacrylate fuming is one of the most commonly used techniques for the detection of fingerprints on non-porous substrates. However, it cannot be directly compared to SiO₂ nanoparticles since the obtained results are not luminescent. In order to avoid overestimating results and introducing a bias toward one technique or the other, a luminescent technique should therefore be used to offer a valid comparison. Luminescent marks can be obtained using conventional cyanoacrylate by following a two-step procedure consisting in fumigating the samples first, then dye-staining them with a luminescent dye dissolved in a solvent [38]. However, to avoid tedious staining procedures and to obtain more homogeneous results throughout the sample sets, a one-step luminescent cyanoacrylate was privileged during this study: the LumicyanoTM [37]. The obtained marks offer luminescent

304 properties either under UV (326 nm) or at 511 nm and the results can be observed with an
305 emission band centred at 562 nm. It however appeared that good luminescent marks could be
306 observed under the same conditions used for RuBpy (i.e. excitation at 495 nm and emission
307 filter at 590 nm). Using the same visualisation conditions help to image both sides at the
308 same time and to keep constant parameters for comparison.

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

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

332 Regarding black PE, the previous observations were still valid (Figure 5 – second column).
333 Cyanoacrylate luminescence was less intense and led again to dotted marks. For donor B, the
334 marks were barely visible. The background noise observed with SiO₂ on aluminium foil is
335 much more pronounced on PE. Sometimes it concealed the marks almost entirely (donors A
336 and B). It was however not homogeneous and when absent it became possible to observe
337 luminescent marks of high quality with clear level 3 features (donor C). Nanoparticles were

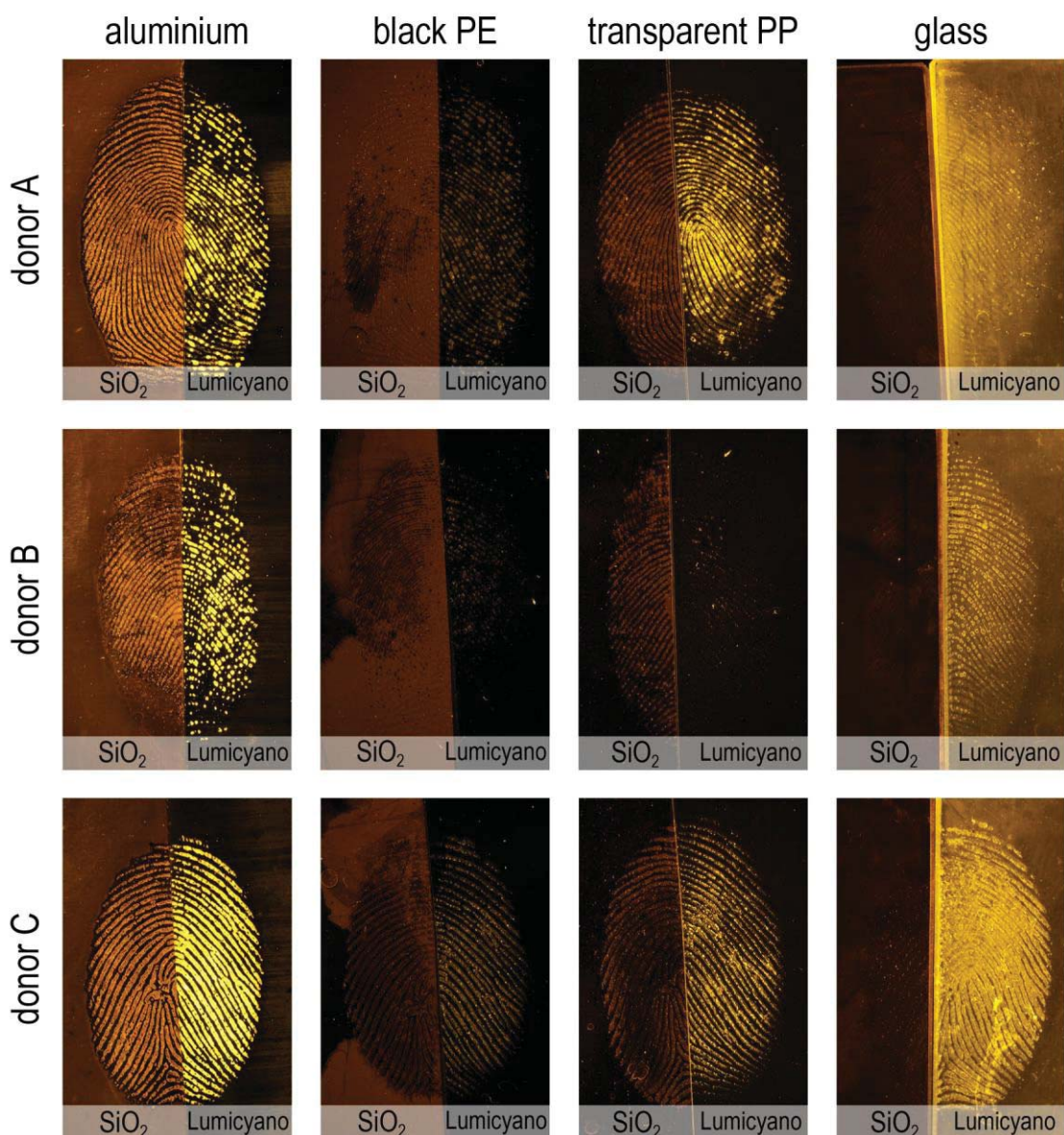
338 thus effectively attracted on the secretions, but the ridges were partially covered by a non-
339 selective deposition onto the surface. That reinforces the needs of further studies on the
340 interaction with substrates.

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

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

353 In summary, for the first marks of the depletion series, cyanoacrylate succeeded in detecting
354 marks on all tested surfaces. However, differences in quality were consistently observed
355 between donors. These variations can be attributed to the quantity and quality variation
356 among donors' secretions. However, this trend was less pronounced with SiO₂ nanoparticles
357 that react not with specific compounds of the secretion, but with specific functional groups.
358 The results quality was however more tightly related to the substrate type, which indicates
359 that the detection conditions can be further adjusted. Glass appeared to be a challenging
360 surface since nanoparticles solution tended to wash the secretion, and thus failing in detecting
361 any mark. Moreover, background staining appeared on black PE, impinging the detection of
362 the marks. Future optimisations need to be carried on, especially to decrease the unwanted
363 background staining and to obtain a more versatile technique that could be applied on a wider
364 range of substrates. SiO₂ nanoparticles application remains promising since the obtained
365 results are very homogeneous and appeared to be less donor-dependent. This, in itself,
366 represents a considerable advantage over cyanoacrylate fuming.

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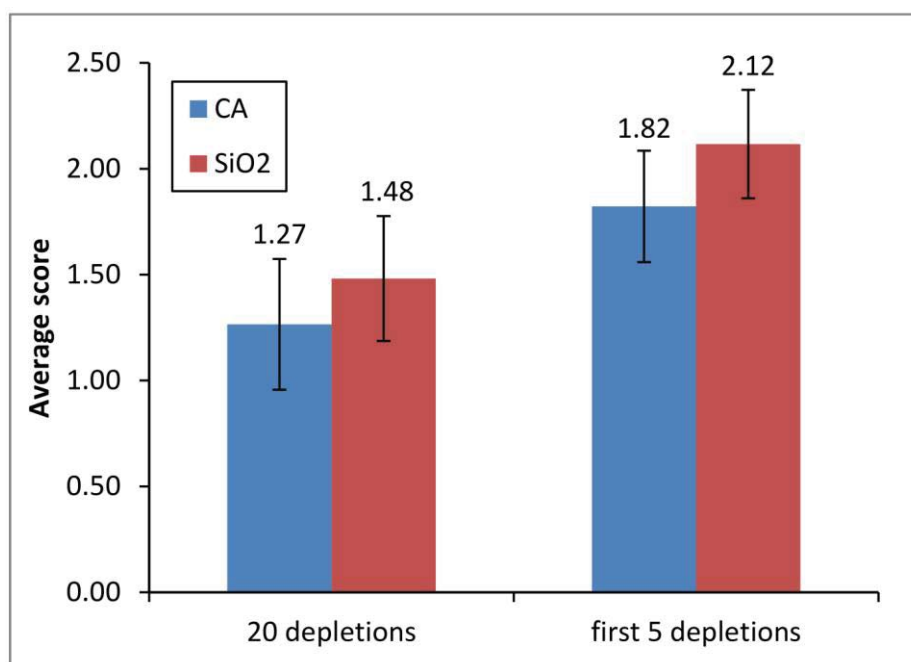
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369 Figure 5: Comparison of fingerprints detected with RuBpy-doped silicon oxide nanoparticles
 370 (left halves) and Lumicyano™ (right halves) from three donors on four substrates.
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372 Results obtained with the depletive series are presented below. On average, by taking into
 373 account every mark from each donor and substrate, comparable scores were obtained for both
 374 techniques (1.3 for Lumicyano™ and 1.5 for SiO₂ nanoparticles) (Figure 6). When only the
 375 first five depletions were considered, a general increase of scores was noticed (1.8 for
 376 Lumicyano™ and 2.1 for SiO₂ nanoparticles), showing that nanoparticles gave slightly better
 377 results on average (Figure 6).

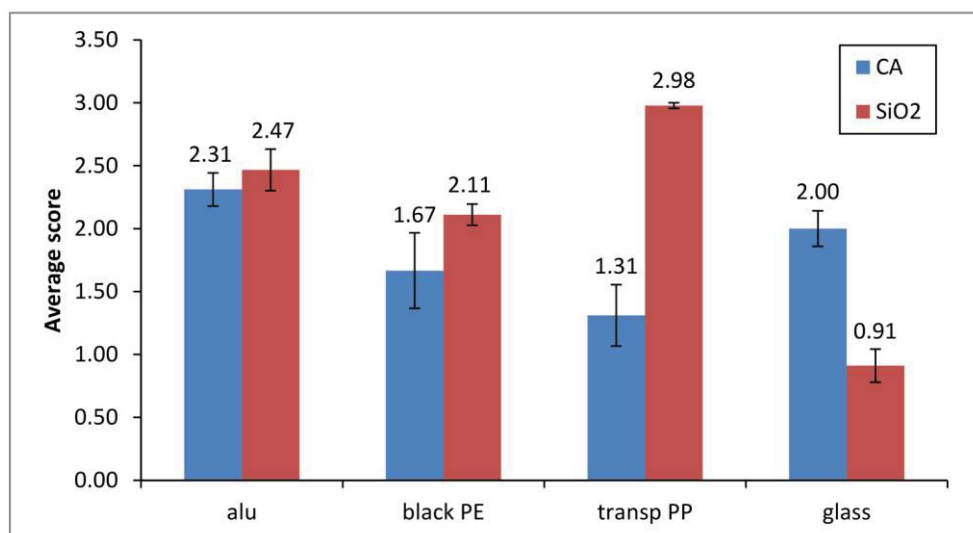
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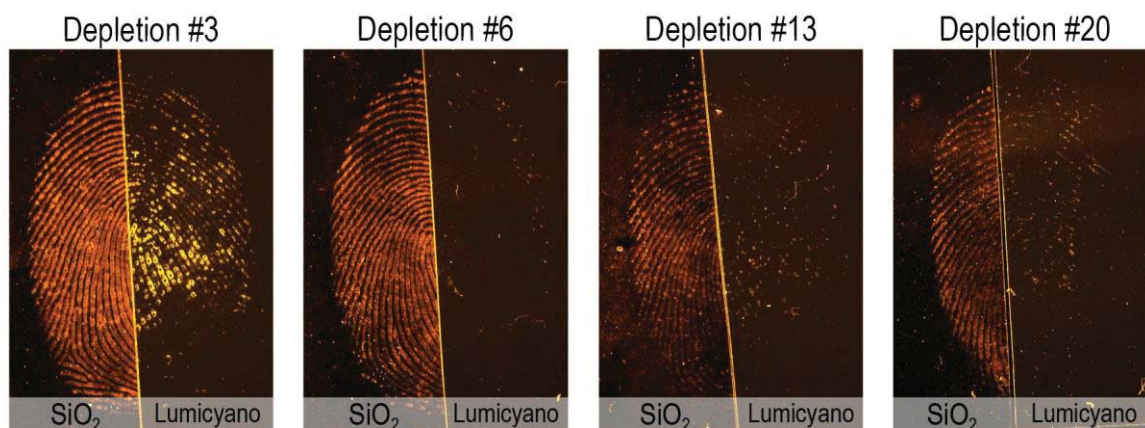
380 Figure 6: Comparison of the average results obtained with LumicyanoTM (CA) and RuBpy-
 381 doped SiO₂ nanoparticles.
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383 By looking at each substrate separately and considering only the first five depletions, results
 384 can be described in more details (Figure 7). On aluminium foil, equivalent results were
 385 obtained showing that both techniques performed well, but on glass, as described above, SiO₂
 386 solution tends to wash the marks, leading to low quality results, cyanoacrylate fuming shows
 387 superior scores. For the black PE, even if background staining was observed, the average
 388 quality was still superior for SiO₂ nanoparticles compared to cyanoacrylate. The biggest
 389 difference appeared on transparent PP where cyanoacrylate stopped being effective after just
 390 a few depletions, while SiO₂ nanoparticles kept detecting marks. This was not only true for
 391 the first five depletions, good quality results were obtained until the twentieth depletion
 392 (Figure 8).



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



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

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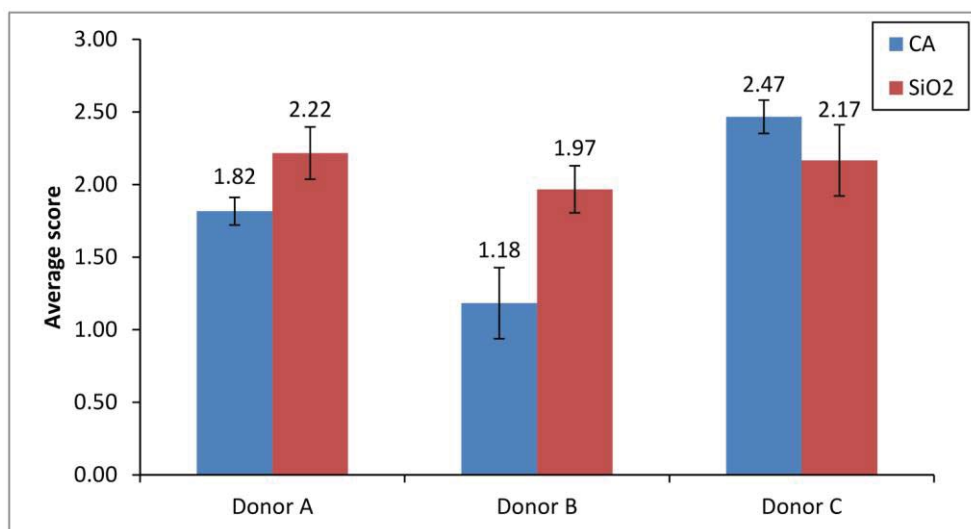
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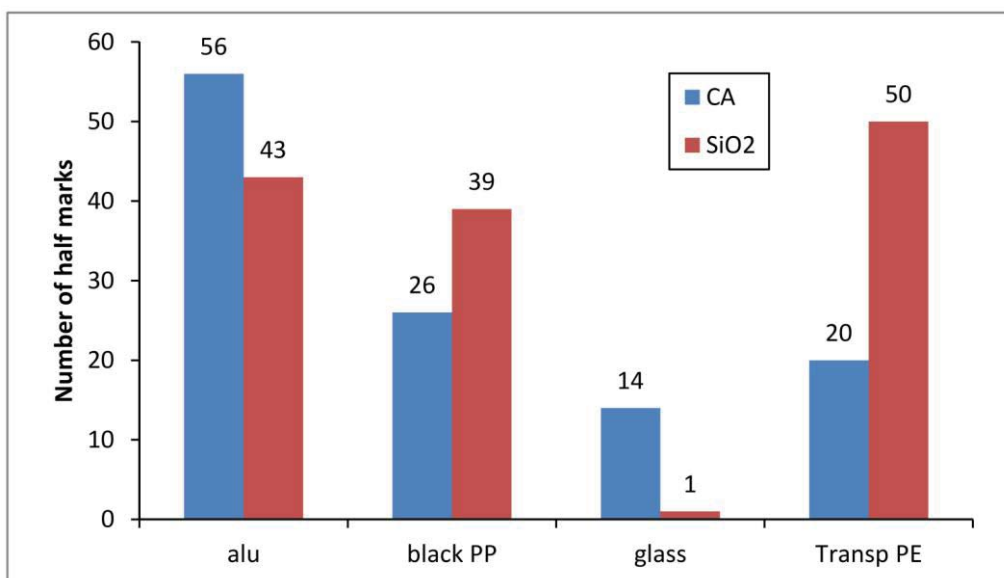
When average scores were calculated considering each donor individually, SiO₂ nanoparticles were less donor dependent than cyanoacrylate (Figure 9). The calculated variance between donors for cyanoacrylate is 0.41, whereas the one for SiO₂ nanoparticles is only 0.02.

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



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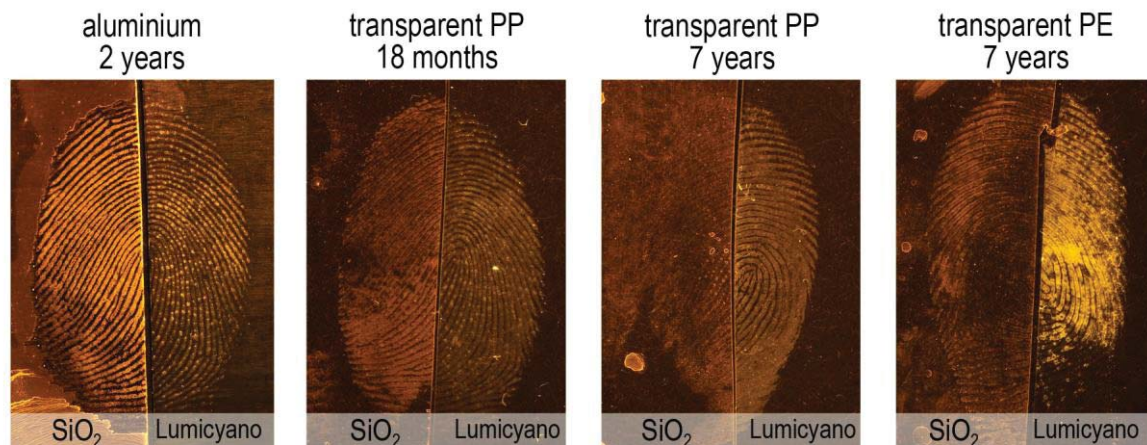
Figure 9: Comparison of the average results obtained from three different donors with Lumicyano™ (CA) and RuBpy-doped SiO₂ nanoparticles.



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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.

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



427

428 Figure 11: Comparison of old fingerprints (18 months to 7 years) detected with RuBpy-
 429 doped silicon oxide nanoparticles (left halves) and Lumicyano™ (right halves) on three
 430 substrates.
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4. Conclusions

434 This paper investigated an application of luminescent functionalised SiO₂ nanoparticles for
 435 fingerprint detection. Several optimisations of the detection protocol for considering dye-
 436 doped SiO₂ nanoparticles as efficient fingerprint reagents were presented. Appropriate
 437 detection conditions, outer functionalisations and luminescent dyes were successively studied
 438 and selected, leading to an optimised protocol. A comparison to Lumicyano™, a one-step
 439 luminescent cyanoacrylate (CA), was then conducted to assess the efficiency of the method.
 440 Both techniques were compared on series of 20 depletive marks from three donors on four
 441 different non-porous substrates.

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

447 Heterogeneous detection results proved that the technique remained to be further optimised.
 448 More work still needs to be undertaken in order to provide a fully operational technique, but
 449 the reported results in this study showed that SiO₂ nanoparticles are very promising and that
 450 research effort should be further pursued.

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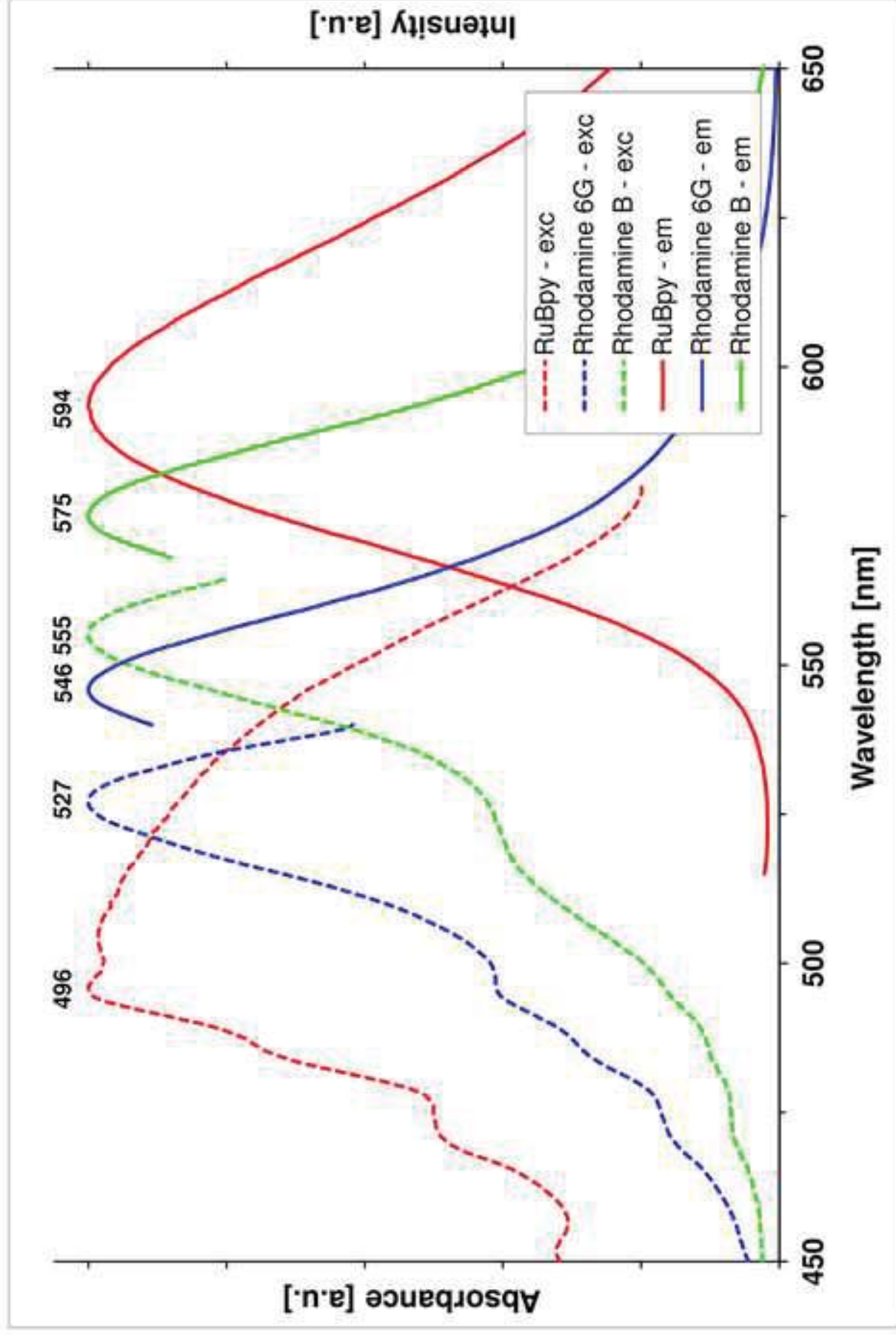


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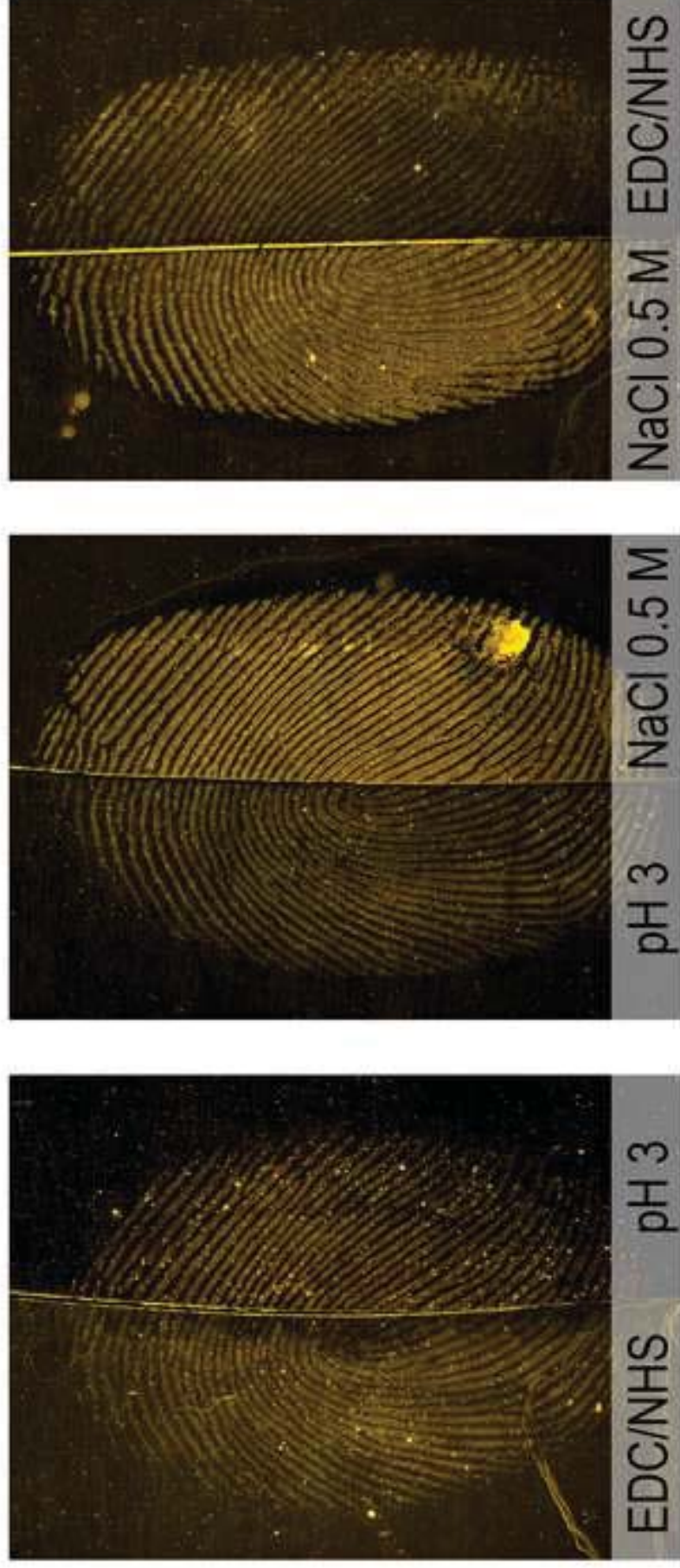


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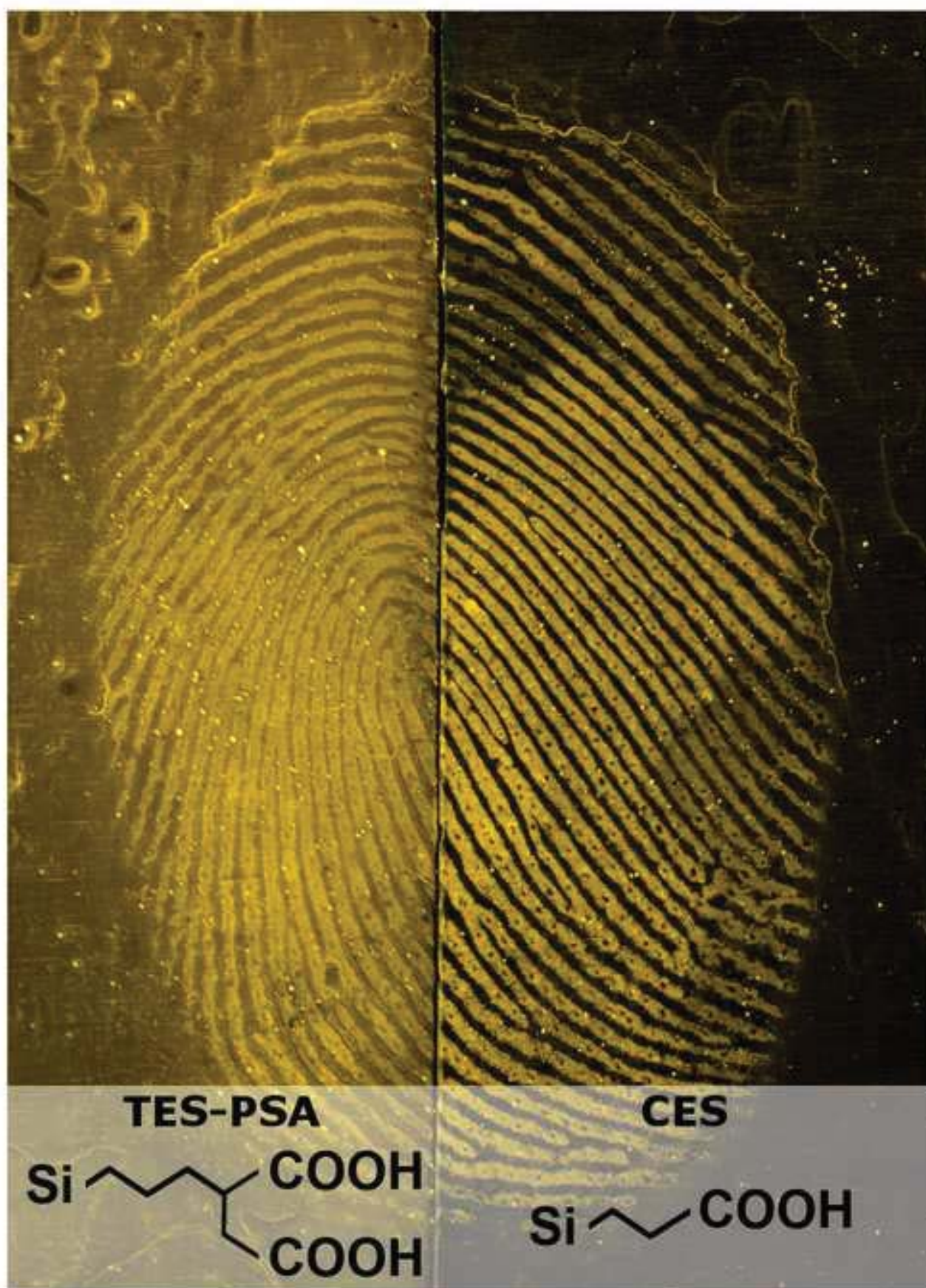


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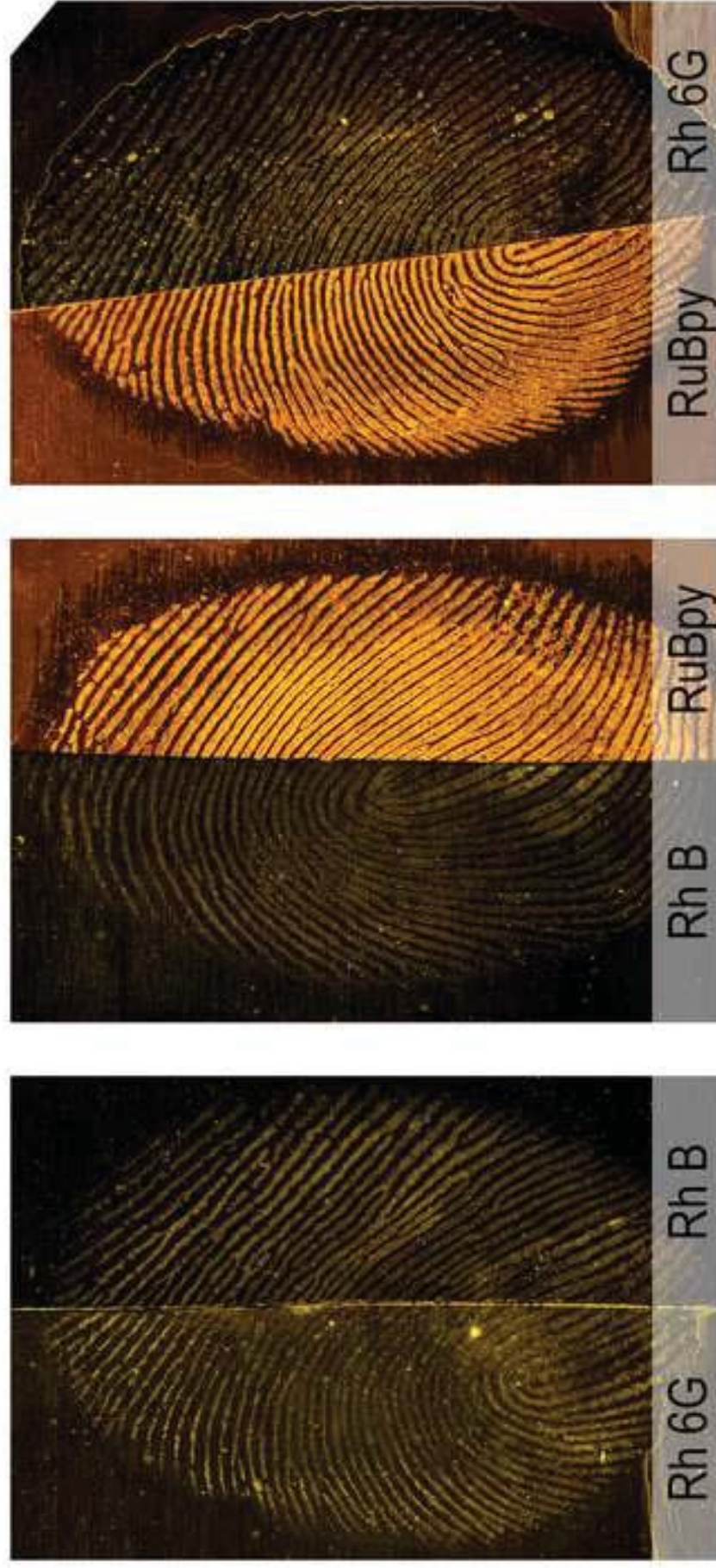


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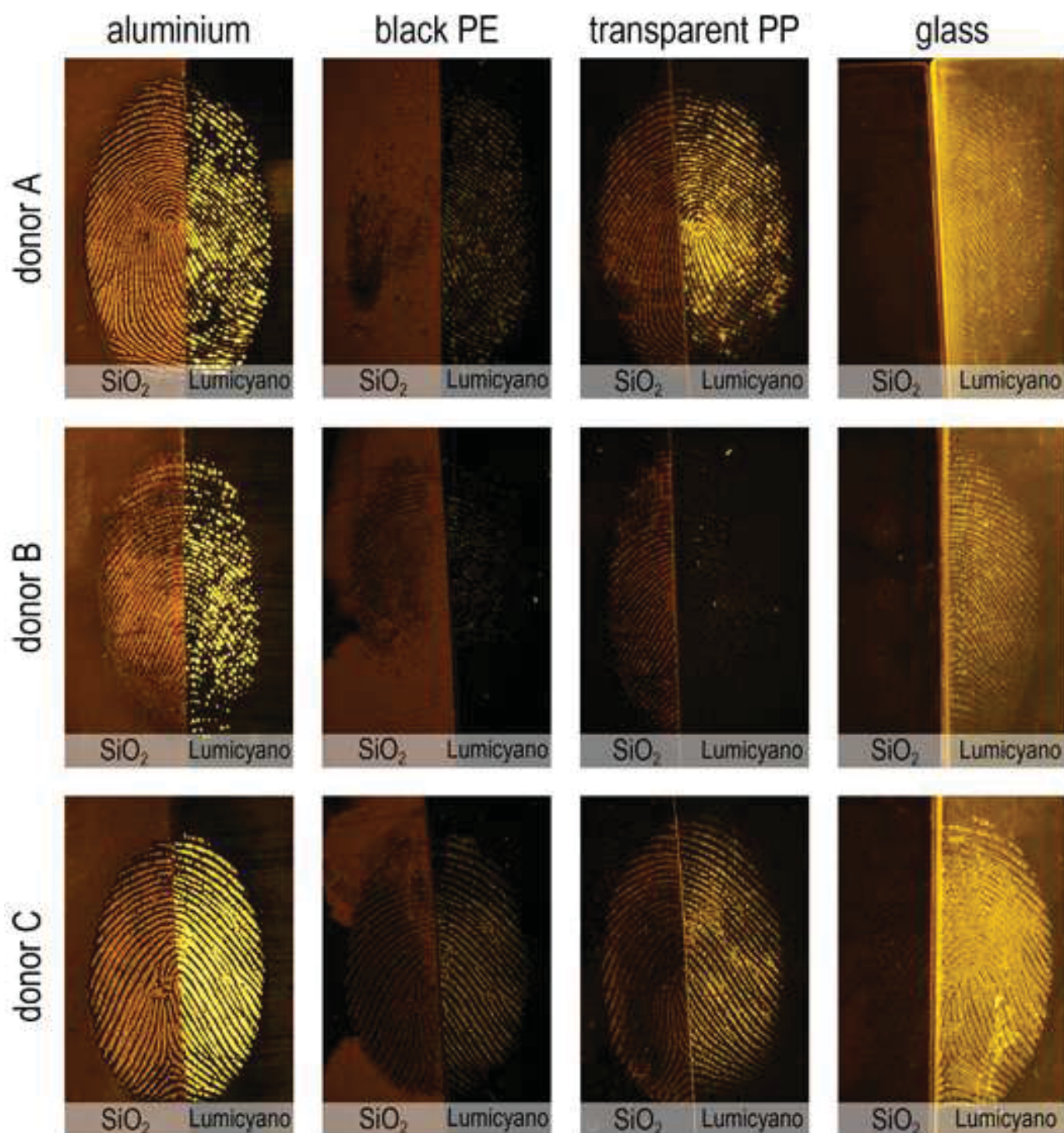


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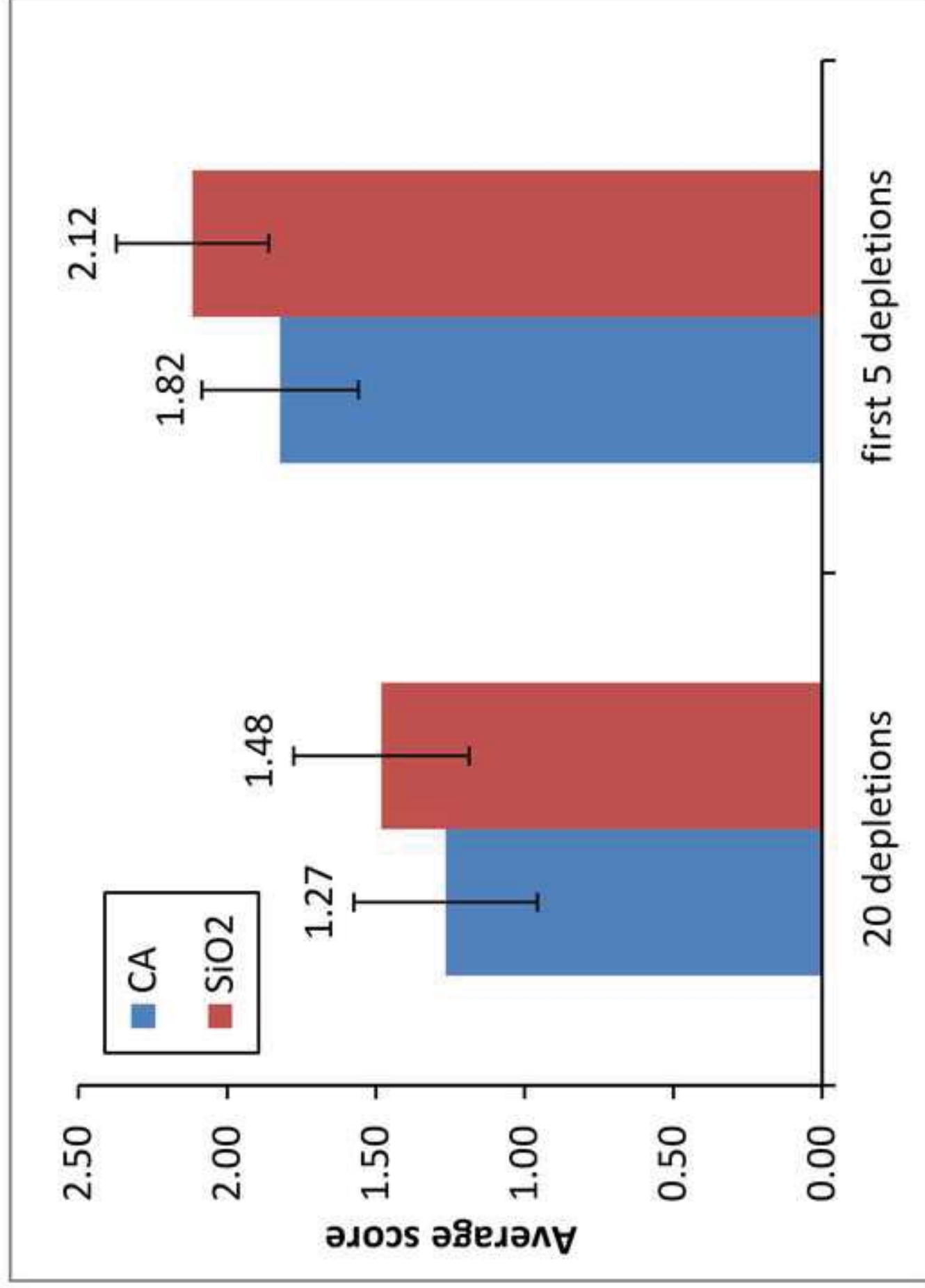


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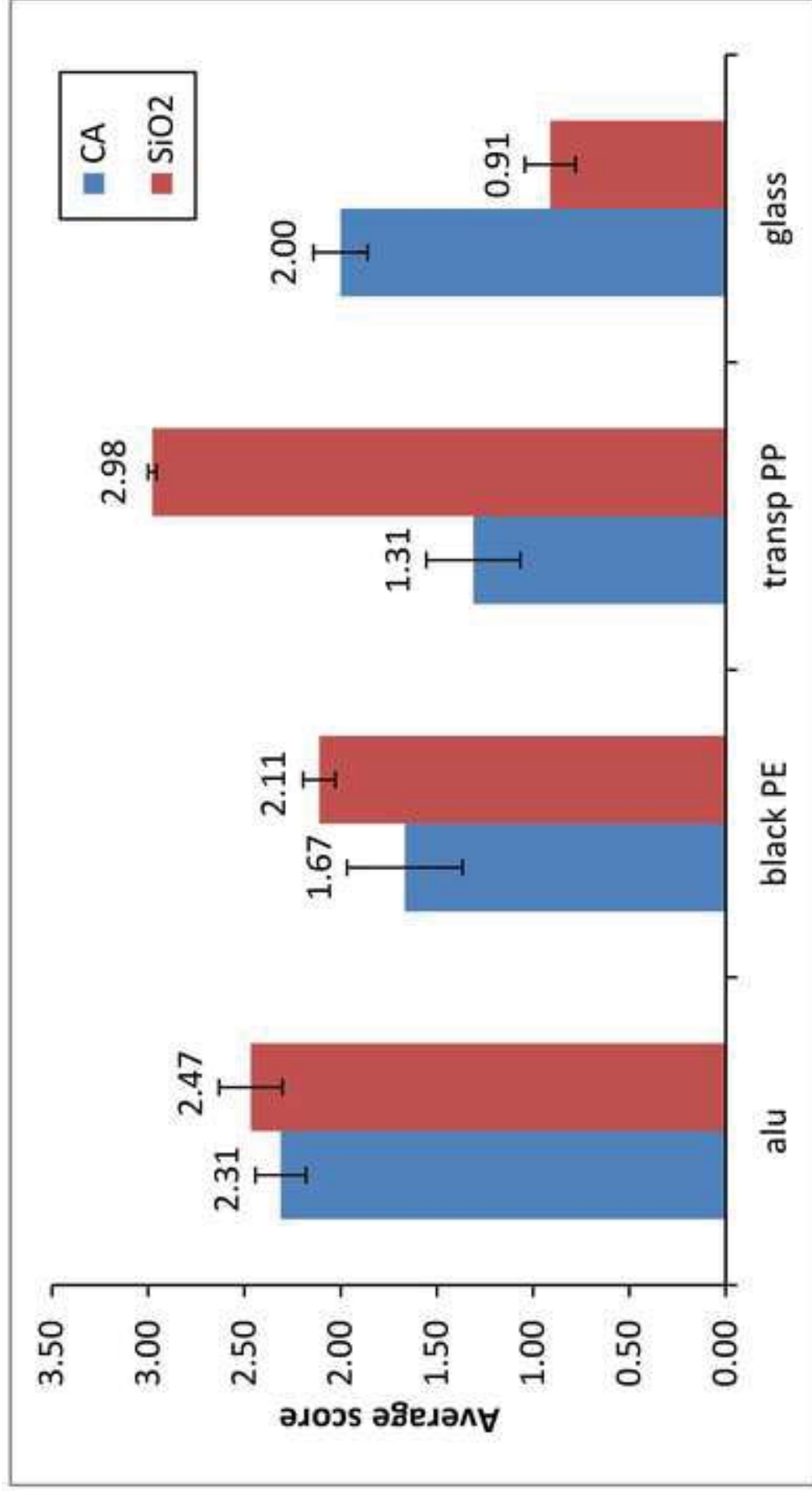


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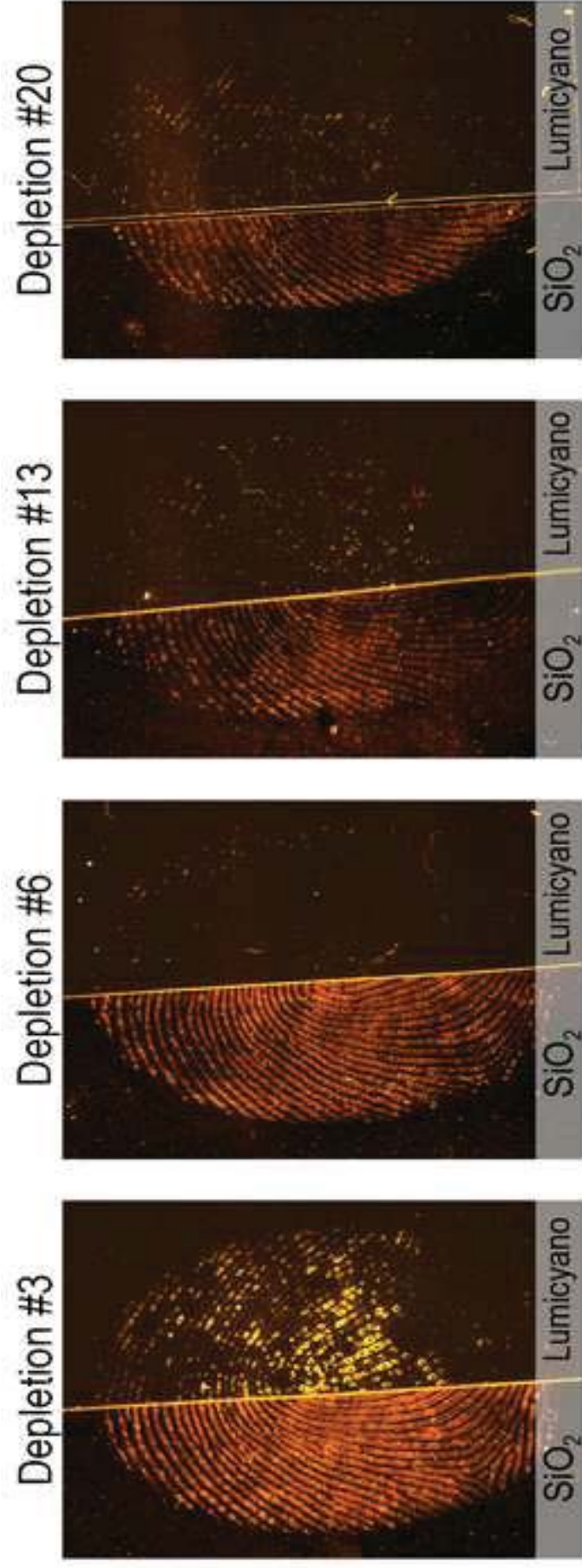


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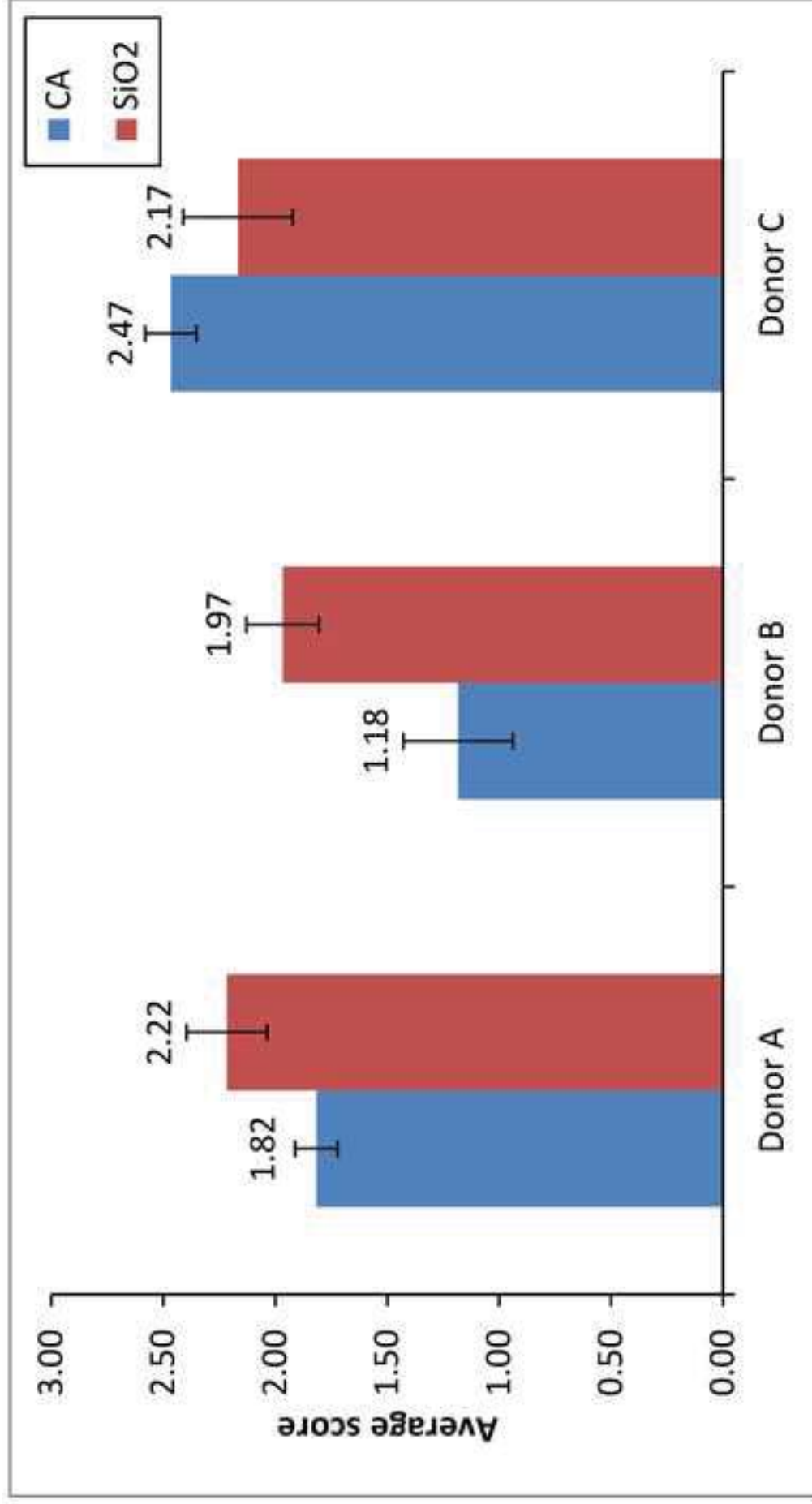


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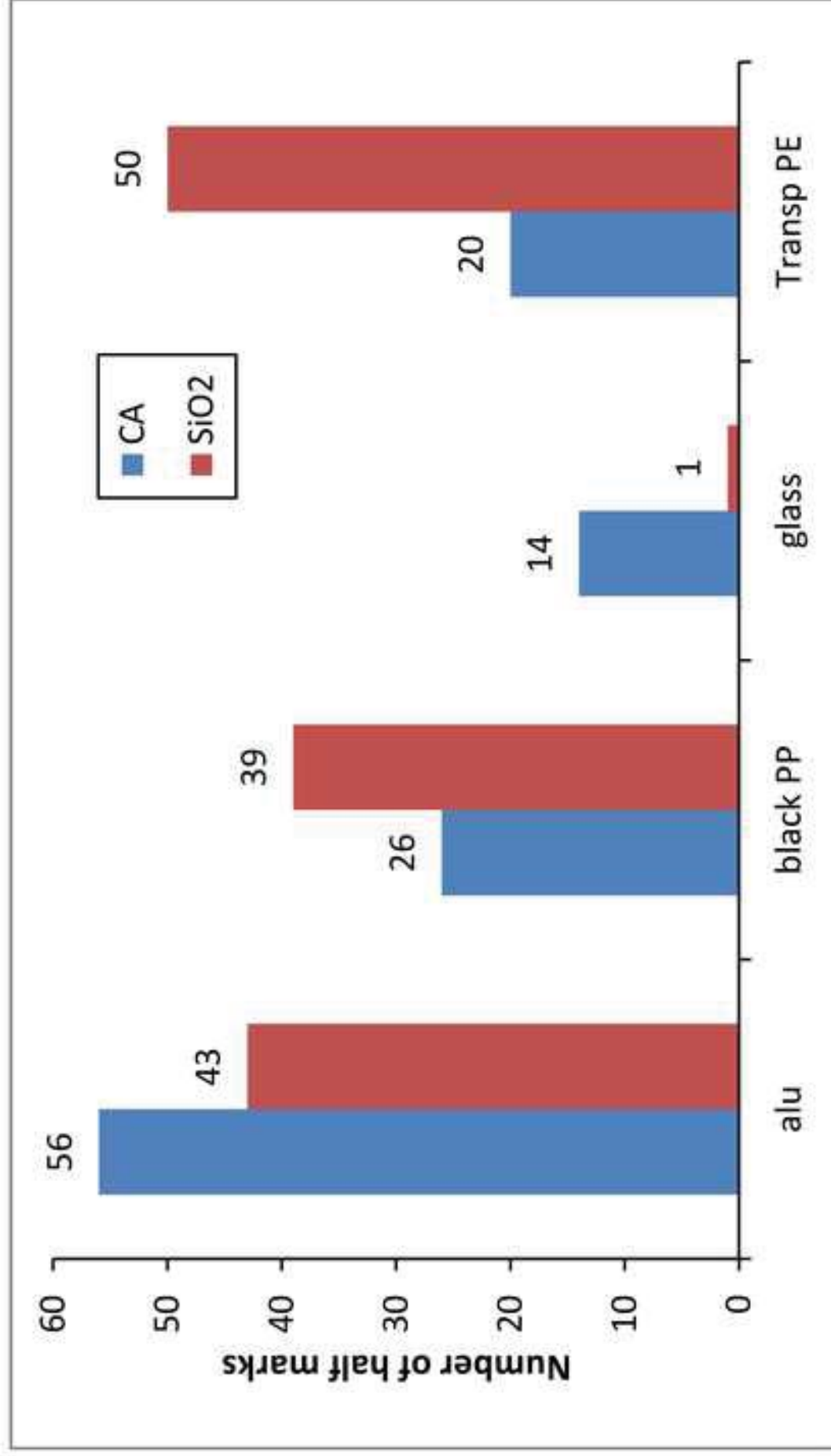


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