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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 a
3 lot of attention. A substantial number of nanoparticle types has thus been studied and applied
4 with varying success. However, despite all efforts, few publications present clear supporting
5 evidence of their superiority over standard and commonly used techniques. This paper
6 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

1. Introduction

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

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

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

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

consequence, SiO₂ nanoparticles could present an almost unlimited range of functional groups. Dye molecules can be entrapped within the siloxane matrix during the synthesis, providing a wide range of optical properties. Various synthetic procedures exist, but two of them are most commonly considered: the Stöber's synthesis and the reversed micro-emulsion. The Stöber's synthesis [28] leads to bulk production, but the size and surface controls are limited. On the other end, reversed micro-emulsion [29] enables to accurately control size, optical properties and functionalisation all at the same time, but with a lower yield.

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

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

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

2. Materials and methods

2.1 Synthesis and functionalisation of SiO₂ nanoparticles

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

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

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

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.

2.2 Characterisation of the nanoparticles

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

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

2.3 Fingerprint sampling

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

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

2.4 Fingermark detection

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

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

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 fingermark 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

Nanoparticles solutions obtained via micro-emulsion were stable for months when stored at 4 °C in a fridge. 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 covered three distinct areas of the spectrum. They also have been used in previous studies [30-32].

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

3.2 Detection mode

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

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

Figure 2: Comparison between three application modes of Rhodamine 6G-doped SiO_2 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).

3.3 Surface functionalisation

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

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

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 fingerprints. 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).

3.4 Luminescence properties

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

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

Figure 4: Comparison between SiO_2 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).

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.

3.5 Comparison with cyanoacrylate fuming

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 SiO_2 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 properties either under UV (326 nm) or at 511 nm and the results can be observed with an emission band centred at 562 nm. It however appeared that good luminescent marks could be observed under the same conditions used for RuBpy (i.e. excitation at 495 nm and emission filter at 590 nm). Using the same visualisation conditions help to image both sides at the same time and to keep constant parameters for comparison.

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

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

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

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

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

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

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

Figure 5: Comparison of fingerprints detected with RuBpy-doped silicon oxide nanoparticles (left halves) and Lumicyano™ (right halves) from three donors on four substrates.

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

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396

397 Figure 6: Comparison of the average results obtained with LumicyanoTM (CA) and RuBpy-
398 doped SiO₂ nanoparticles.
399

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

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

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

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.

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

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

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.

444

445 Figure 11: Comparison of old fingermarks (18 months to 7 years) detected with RuBpy-doped
 446 silicon oxide nanoparticles (left halves) and LumicyanoTM (right halves) on three substrates.
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448

449 4. Conclusions

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

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

463 Heterogeneous detection results proved that the technique remained to be further optimised.
 464 Regarding health and safety issue about SiO₂ nanoparticles application, no toxicity assessment
 465 of the synthesized nanoparticles was performed in this study. This should be considered in
 466 details before any large scale application. More work still needs to be undertaken in order to
 467 provide a fully operational technique, but the reported results in this study showed that SiO₂
 468 nanoparticles are very promising and that research effort should be further pursued.

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