

# **Nanoparticles for fingerprint detection: an insight into the reaction mechanism**

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**Abstract.** This publication presents one of the first use of silicon oxide nanoparticles to detect fingerprints. The study is not confined to showing successful detection of fingerprints but is focused on understanding the mechanisms involved in the fingerprint detection process. To gain such an understanding, various chemical groups are grafted onto the nanoparticles surface, and parameters such as the pH of the solutions or zeta potential are varied to study their influence on the detection. An electrostatic interaction was the generally accepted hypothesis of interaction between nanoparticles and fingerprints, but the results of this research challenges that hypothesis, showing that the interaction is chemically driven. Carboxyl groups grafted onto the nanoparticles surfaces react with amine groups of the fingerprint secretion. This formation of amide linkage between carboxyl and amine groups has further been favoured by catalysing the reaction with a compound of diimide type. The research strategy adopted here ought to be applicable to all detection techniques using nanoparticles. For most of them the nature of the interaction remains poorly understood.

**Keywords.** Forensic science, fingerprint detection, detection mechanism, silicon oxide, electrostatic interaction, chemical reaction, luminescence.

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## 1. Introduction

Following the same trend affecting most scientific and technical disciplines, nanotechnology has also an impact on forensic science. This is especially true for the detection of fingermarks on potentially touched items for which researchers have been very active for more than a decade [1-3] motivated by the fact that a substantial number of fingermarks (estimated to 50% on porous surfaces [4]) remains undetected.

Before that trend in nanoparticles research, numerous detection techniques have been developed to target the various components of the fingermark residue (*e.g.* amino acids [5] or lipids [6]). However, there still exists a lack of sensitivity and selectivity (ability to target specific component of the residue aside from the underlying substrate [7]). Nanoparticles (NPs) are then proposed as a way to tackle these issues. Their low size, their versatility and the ability to specifically tune their surface properties are the main reasons why they attract so much attention [8]. The surface modification versatility of these materials may lead to precise targeting of compounds present in the residue [9], and thus increasing the selectivity [10]. Their various optical properties can lower the detection limits, and improve the sensitivity, typically by using luminescent properties to get rid of background interference.

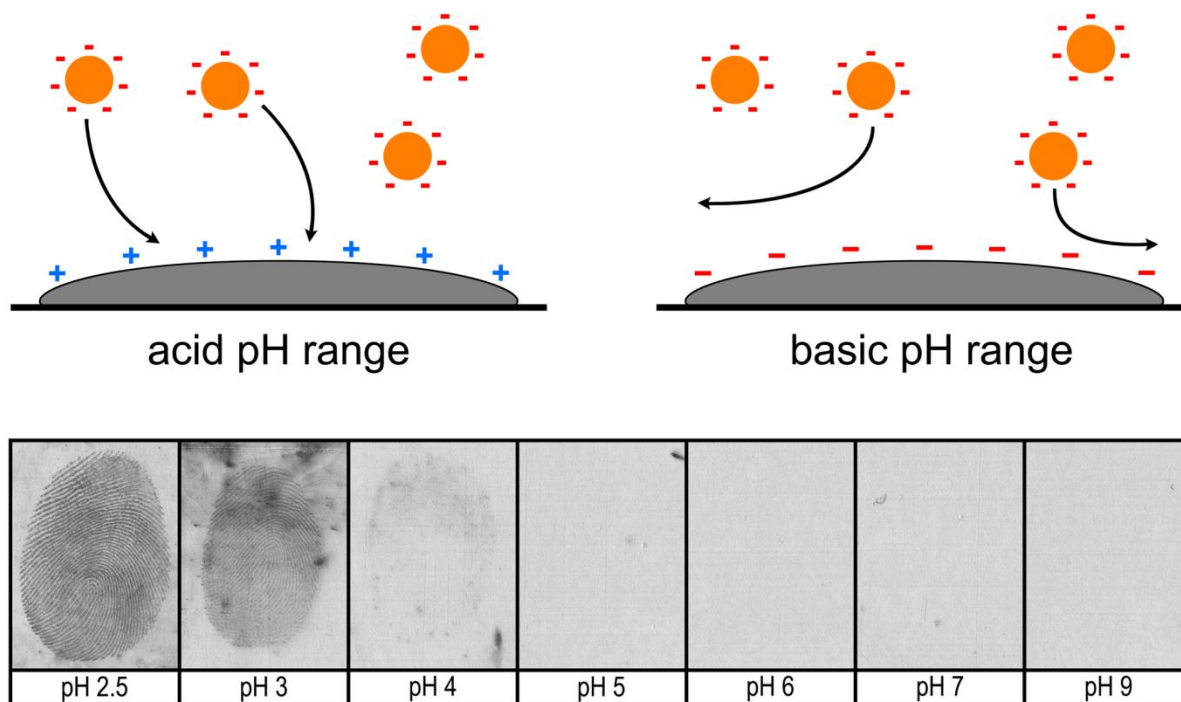
Many types of NPs have been investigated in this context: metal oxide [2], gold [11], silver [12], silicon oxide [13] and semiconductors (such as quantum dots [14]) to cite a few. These NPs can be applied either as dried powders or in suspension (aqueous or organic solvent) by immersion of the item. Powdering mostly relies on physical processes. For example, oleylamine-stabilized gold NPs powdered on fingermarks led to successful detection due to the affinity of the aliphatic functionalized NPs with the fingermark residue (sweat, sebum or other contaminants) [15]. This application suffers from a lack of selectivity as well as major health and safety issues. The use of a suspension however promotes physico-chemical and chemical interactions with the residue. For example, successes have been obtained with gold NPs functionalized with aliphatic chains and suspended in petroleum ether [16], or with gold colloids surrounded by citrate ions in aqueous solution [17].

However very few is known about the precise mechanisms involved in the interaction between the NPs and the fingermark residue. One cause for the paucity of research is the complexity of the residue

which is composed in part from sweat produced by eccrine glands (98% of water, amino acids, proteins, glucose, urea and inorganic ions), fatty compounds excreted by the sebaceous glands (*e.g.* fatty acids, wax esters, squalene) and contaminants (*e.g.* cosmetics, dirt or blood) [18, 19]. Besides the complexity of the residue, *in situ* studies of fingerprints are strongly limited due to the low quantity of material, the low thickness of material and the overall fragility of the secretion residue. Another reason can be found in the research strategies that are focused on the premature application of NPs (often in the form of powder) rather than on the study of fundamental principles involved in the detection process. This leads to publications of techniques supported by empirical optimizations, only, with considerable variations from one publication to the other even for the same type of NPs. An example is the use of cadmium telluride quantum dots (CdTe QDs), for which two papers describe opposite detection conditions [14, 20]. The results obtained so far with NPs are consequently not optimal.

The present work aims at proposing a better understanding of the interactions occurring between NPs and fingerprints. To achieve that objective this research focused on one existing technique – the multimetal deposition (MMD) [21] – based on gold NPs in aqueous solution and for which a suggested mechanism based on electrostatic interaction is commonly accepted [10]. The MMD relies on a two-steps process. First, gold NPs of a size ranging from 14 to 30 nm are attracted on secretion at acidic pH. Second, a selective reduction of silver [17] or gold [22] on the deposited NPs allows to enhance the contrast, and by the same way leads to the fingerprint visualization.

The initial deposition of gold NPs on the fingerprint residue is known to be sensitive to the pH of the colloidal gold solution, with a very narrow effective pH range (around 3). The commonly accepted theory states that at acidic pH range, secretions are positively charged due to the protonation of amine groups (amino acids, proteins). NPs are in turn negatively charged due to citrate ions adsorbed on their surfaces. Colloids are then attracted onto secretions, allowing fingerprints to be detected [11, 23, 24] (figure 1). The narrow pH range is a best-so-far equilibrium between negatively charged NPs and positively charged fingerprints. Although this hypothesis is widely accepted, it has never been demonstrated.



**Figure 1.** Schematic illustration of the electrostatic interaction hypothesis. At acid pH, NPs (negatively charged) are attracted onto fingermark secretions (positively charged). At basic pH, both NPs and fingermark residues are negatively charged, hindering the detection, as illustrated experimentally.

Silicon oxide NPs ( $\text{SiO}_2$  NPs) were preferred to gold nanoparticles to explore the underpinning mechanisms. Contrary to gold NPs,  $\text{SiO}_2$  NPs offer versatile surface modification abilities combined with extended optical properties (*e.g.* by introducing a dye in their inner structure) [13, 25, 26].  $\text{SiO}_2$  NPs can thus be used as a tool to systematically investigate the interactions occurring with the fingerprints.

## 2. Experimental methods

### 2.1. Synthesis of functionalized silicon oxide nanoparticles and characterization

Tetraethyl orthosilicate (TEOS), Triton X-100 (TX-100), cyclohexane, n-hexanol, ammonium hydroxide (25 wt %), rhodamine 6G, sodium chloride (NaCl), *N*-ethyl-*N'*-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS), propionic acid and 3-(trihydroxysilyl)propyl methylphosphonate monosodium salt solution were purchased from Sigma-

Aldrich. Carboxyethylsilanetriol sodium salt, 3-(trihydroxysilyl)-1-propanesulphonic acid and 3-(triethoxysilyl)-propylsuccinic anhydride were purchased from Abcr GmbH & Co. All chemicals were used as received without further purification.

SiO<sub>2</sub> NPs were synthesized by the microemulsion method described by Wang *et al.* [27]. The protocol was followed without any modifications, except the incorporation of the dye: dual rare earth luminophores were replaced by rhodamine 6G. The water-in-oil microemulsion was obtained by successively mixing 3.54 mL of TX-100, 15 mL of cyclohexane, 3.6 mL of n-hexanol and 960 µL of a 0.1 M rhodamine 6G. After stabilization of the micro-emulsion, NPs formation was initiated by adding 200 µL of TEOS, followed by 120 µL of ammonium hydroxide. The mixture was kept under stirring for 24 h.

The prepared SiO<sub>2</sub> NPs were functionalized directly in the micro-emulsion. 50 µL of TEOS and 170 µmol of the selected silane coupling agent were added to the mixture. After another 24 h, a large excess of ethanol was added to destabilize the system. NPs were collected by centrifugation (3500 RCF for 10 minutes) and washed twice with ethanol and then re-dispersed in 20 mL of RO/DI water (18.2 Ω·cm).

NPs hydrodynamic diameter was measured by dynamic light scattering (DLS) and zeta potential ( $\zeta$ ) was determined by laser Doppler micro-electrophoresis, both on a Zetasizer Nano ZS (Malvern Instruments Ltd.). For each sample, the hydrodynamic diameter was measured five times while the  $\zeta$  was measured three times. In both cases, average data were used. To determine the behaviour of the SiO<sub>2</sub> NPs over pH range, pH was adjusted by adding NaOH or HCl to the solutions. Each obtained values was then plotted showing both hydrodynamic diameter and  $\zeta$  evolutions.

Photoluminescence properties of the NPs solutions were measured at room temperature on a Hitachi F-2500 fluorescence spectrometer. All measurements were made on samples obtained after re-dispersion of the SiO<sub>2</sub> NPs in water.

## 2.2. Fingerprint deposition

The study is specifically designed to better understand fundamental principles of the interaction between NPs and fingerprints. Therefore only one substrate and one donor were chosen. Aluminum foil has been selected as an ideal substrate. A donor known as “good” was selected in order to have a sufficient amount of natural secretions. Fingerprints were deposited on aluminum foils following a standard procedure consisting in successive apposition of the right thumb, index, middle and ring finger. These marks were considered as naturally mixed, containing both eccrine and sebaceous secretions. The only restriction was that the donor has not washed his hands at least one hour before deposition and behaved normally in the meanwhile. To prevent deposition of overloaded marks, the donor was not asked to rub his fingers on his face before deposition, but only to rub his hands together in order to homogenize the already-present secretions. The fingerprints samples were finally stored in dark for at least three weeks before being processed. The delay between the fingerprint deposition and the treatment of samples was critical. The three-week delay was chosen in order to avoid a “fresh mark effect”, giving misleading or not representative results.

### *2.3. Fingerprint detection and recording*

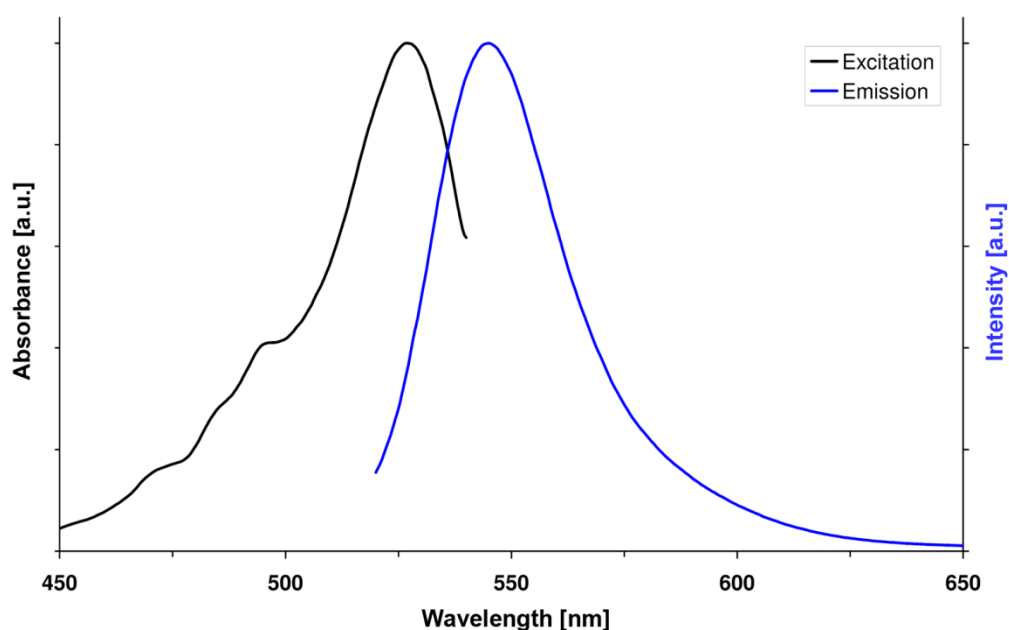
Before processing, the SiO<sub>2</sub> NPs solutions were diluted by two with RO/DI water and the pH was adjusted with either NaOH or HCl solutions, depending on the desired pH range. The solution was then poured in a dish. The amount of solution must be sufficient to cover the bottom of the dish. The samples were deposited on the surface of the solution with fingerprints facing down and then let float for one hour without stirring. After treatment, the aluminum foils were rinsed in deionized water to wash away the non-bounded NPs.

For the detection solution containing EDC/NHS, the detection conditions have been optimized with a pH set at 6. The SiO<sub>2</sub> NPs solutions were diluted by four with RO/DI water and the immersion time reduced to 30 minutes.

Once dry, the samples were observed in luminescence mode, *i.e.* with an excitation at 495 nm and an observation filter with a band pass centred at 590 nm. Each result was recorded under the same illumination conditions and with the same camera settings. No other specific digital enhancements were performed.

### 3. Results and discussion

Silicon oxide nanoparticles ( $\text{SiO}_2$  NPs) were synthesized by reverse microemulsion method, allowing to graft chosen functional groups onto the NPs surface [28-30]. An organic dye, rhodamine 6G, was introduced within the structure to provide luminescent properties to NPs. Excitation and emission spectra of the doped  $\text{SiO}_2$  are shown in figure 2. Dynamic light scattering (DLS) was used to characterize the obtained NPs (such as hydrodynamic diameter and zeta potential intensity). An average diameter of  $70 \text{ nm} \pm 2 \text{ nm}$  was obtained.



**Figure 2.** Excitation and emission spectra of a silicon oxide nanoparticles aqueous solution, doped with rhodamine 6G.

Detailed synthetic procedures, fingerprints collect and storage, as well as detection protocols and fingerprints recording are available in the "Experimental Methods" section.

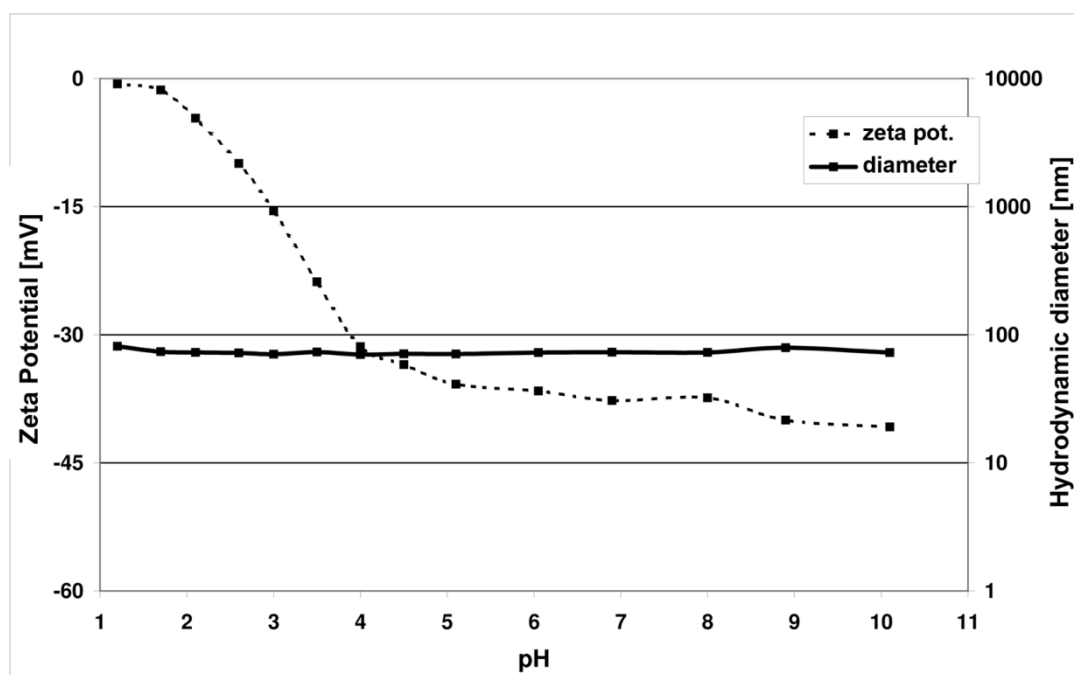
#### 3.1. Implementing the electrostatic interaction

As a starting point,  $\text{SiO}_2$  NPs are used to mimic the physico-chemical properties of the gold NPs used for MMD. Since a major property of gold colloids is the negative charge due to the adsorbed sodium citrate – bearing three carboxyl groups, carboxyethylsilanetriol has been chosen as silane



coupling agent. This molecule possesses a carboxyl group, which provides a negative charge to NPs in alkaline solution. If the detection mechanism is effectively driven by electrostatic attraction, the carboxyl-functionalized SiO<sub>2</sub> NPs (SiO<sub>2</sub>-COOH) are expected to reproduce the affinity of gold NPs for fingerprints at acidic pH.

The obtained SiO<sub>2</sub>-COOH NPs were characterized in terms of size and zeta potential ( $\zeta$ ) according to the pH (figure 3). The measured hydrodynamic diameter, of about 70 nm, remains constant along the pH range. No aggregate formation is detected. Regarding  $\zeta$ , the value is negative over the entire pH range, as expected. Above pH 4, the particles possess a strong negative  $\zeta$  ( $< -30$  mV), which gives a good stability to the solution [31]. Below pH 4, the  $\zeta$  potential increases rapidly to reach a value of zero at about pH 1. This is explained by the protonation of the carboxylic groups.

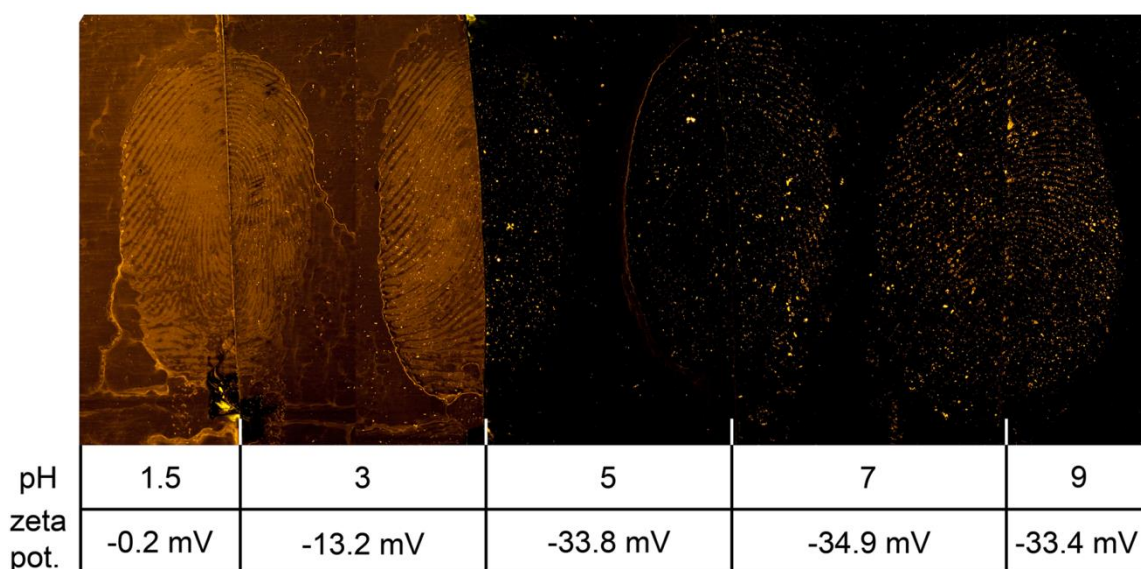


**Figure 3.** Graph showing the pH-dependent evolution of both hydrodynamic diameter and zeta potential of an aqueous solution of SiO<sub>2</sub> NPs functionalized with carboxyl groups.

Figure 4 shows the results of fingerprint detection with SiO<sub>2</sub>-COOH NPs solutions, along the 1.5 to 9 pH range. The fingerprints have been cut in half and processed separately in order to compare the results that can be obtained upon these different parameters. The results are similar to those obtained using gold NPs (figure 1). According to the electrostatic interaction hypothesis, in the pH 5 to 9 range both the secretions and the NPs possess a negative charge which induces a repulsion that hinders the

detection. On the contrary, at pH 3 the secretions are assumed to be positively charged, while NPs still possess a negative  $\zeta$  of approximately -15 mV. The attraction may thus take place, and marks are detected. At pH 1.5, the  $\zeta$  of the NPs is close to zero, whereas the papillary secretions are theoretically more strongly positively charged. The NPs are still attracted onto fingermarks, leading to their visualization.

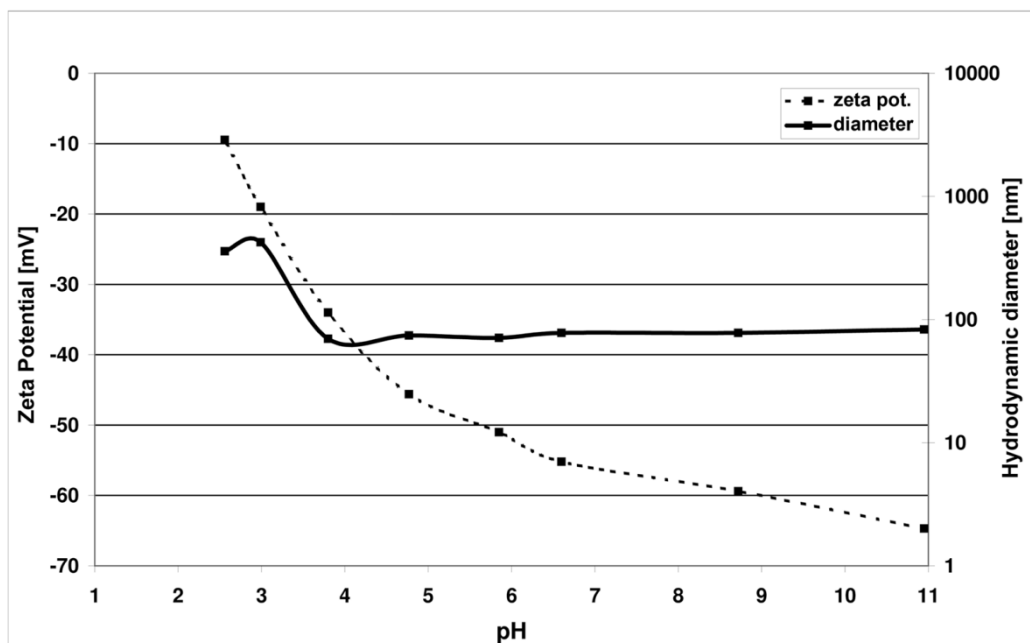
These observations support at this stage the electrostatic hypothesis. If truly this interaction is driven by a compromise between the charges of different entities, it should then be possible to maximize this interaction – and thereby improve the quality of results – by using NPs presenting a strongly negative  $\zeta$  at pH 3.



**Figure 4.** Results obtained after application of SiO<sub>2</sub> NPs functionalized with carboxyl groups, at various pH, on fingermarks deposited on aluminum foils. For values of 5, 7 and 9, no results are visible, whereas for 1.5 and 3, marks are detected.

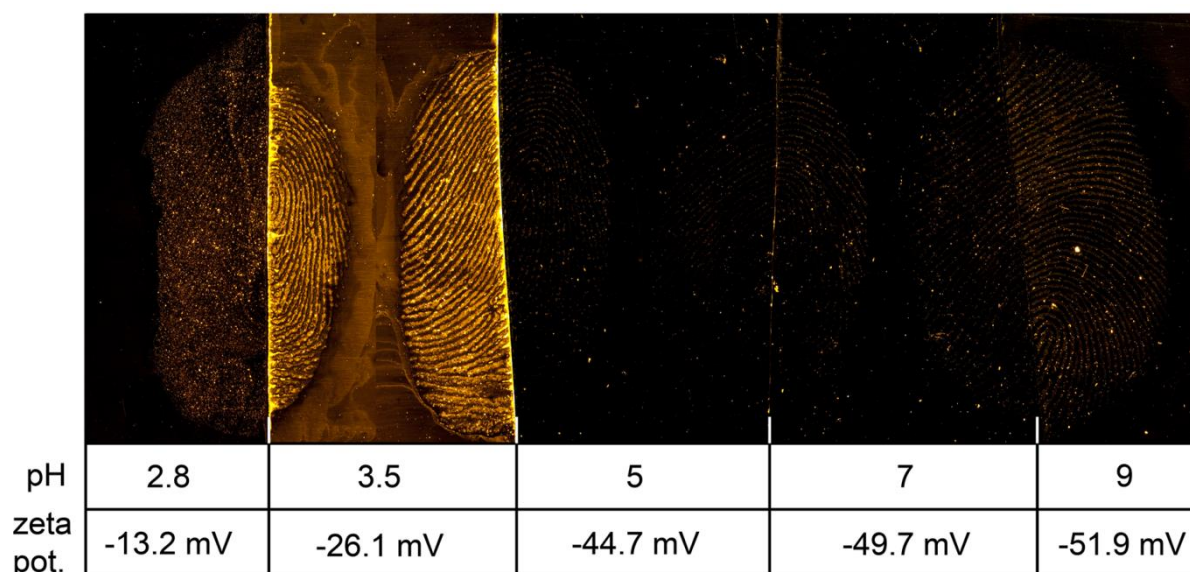
### 3.2. Attempts to maximize the electrostatic interaction

In order to obtain NPs with a stronger  $\zeta$  at lower pH, succinic anhydride functions have been grafted around the SiO<sub>2</sub> NPs (SiO<sub>2</sub>-(COOH)<sub>2</sub>). This functional group is hydrolysed in contact with water and forms two carboxylic groups. DLS analysis shows the physico-chemical properties of these NPs, following the same trend as SiO<sub>2</sub>-COOH (figure 5).



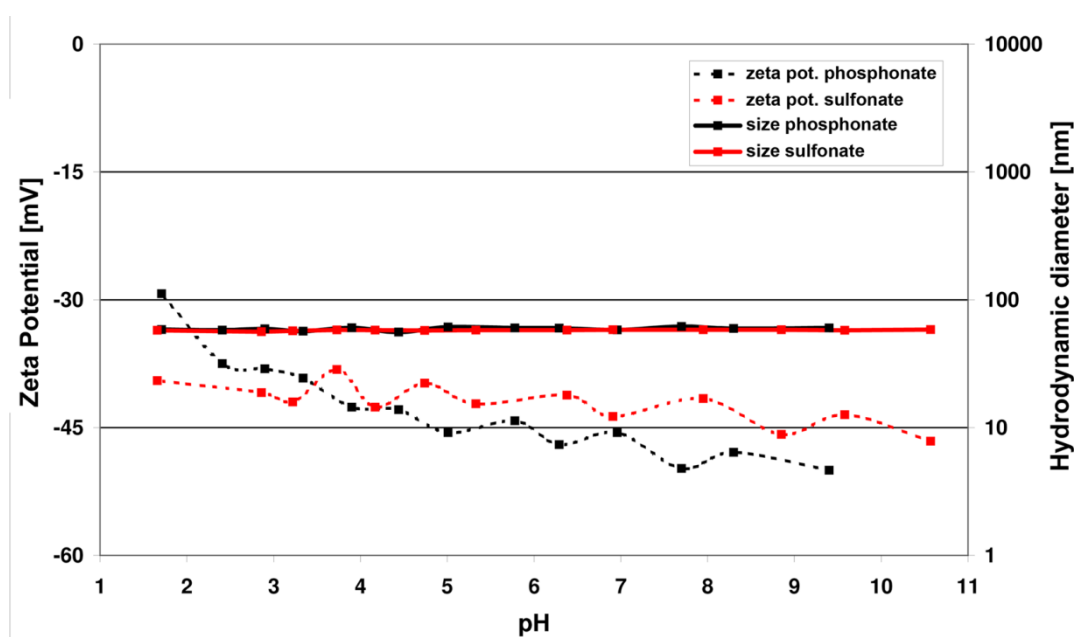
**Figure 5.** Graph showing the pH-dependent evolution of both hydrodynamic diameter and zeta potential of an aqueous solution of SiO<sub>2</sub> NPs functionalized with anhydride succinic groups.

When applied to fingerprints, these NPs behave similarly to the ones bearing a single carboxyl group (figure 6). Above pH 5, no detection occurs. At pH 3.5, luminescent fingerprints are obtained. The  $\zeta$  has a value of -26 mV, which is about 10 units more negative than the  $\zeta$  value measured at pH 3 with SiO<sub>2</sub>-COOH NPs (-13.2 mV). The last result obtained at pH 2.8 cannot be taken into consideration since at this value the solution was not stable and NPs started to aggregate. Therefore, values of pH below 3.5 are not suitable to detect fingerprints with these NPs.






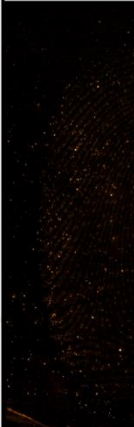






**Figure 6.** Results obtained after application of SiO<sub>2</sub> NPs functionalized with anhydride succinic groups, at various pH, on fingerprints deposited on aluminum foils. For values of 5, 7 and 9, no results are visible. At pH 3.5, marks are detected. At pH 2.8, blurred and weakly luminescent marks are obtained due to NPs instability and aggregate formation.

Two other alternatives to carboxyl groups are methylphosphonate ( $-\text{OP}(\text{O})(\text{ONa})\text{CH}_3$ ) and sulfonate ( $-\text{SO}_3\text{H}$ ) groups. DLS analyses of these two different functionalized NPs show that both solutions are stable and possess a highly negative  $\zeta$  on the entire pH range (figure 7). Figure 8 shows samples treated with these two solutions of strongly-negatively-charged NPs, respectively functionalized with (a) methylphosphonate groups, and (b) sulfonate groups. Unlike the previous results obtained with SiO<sub>2</sub>-COOH and SiO<sub>2</sub>-(COOH)<sub>2</sub>, which allow to detect marks at pH 3, these highly charged NPs have absolutely no affinity with the fingerprint residue, regardless of the pH value.



**Figure 7.** Graph showing the pH-dependent evolution of both hydrodynamic diameter and zeta potential of two aqueous solutions of SiO<sub>2</sub> NPs functionalized respectively with phosphonate and sulfonate groups.

pH	1.5	3	5	7	9
-OPO <sub>2</sub> CH <sub>3</sub>					
pot. zêta	-23.8 mV	-36.9 mV	-42.0 mV	-45.6 mV	-49.1 mV
-SO <sub>3</sub> H					
pot. zêta	-43.0 mV	-46.6 mV	-48.2 mV	-48.2 mV	-52.8 mV

**Figure 8.** Results obtained after application at various pH of SiO<sub>2</sub> NPs functionalized with phosphonate groups (above) and sulfonate groups (below), on fingerprints deposited on aluminum foils. No marks are detected regardless the value of the pH.

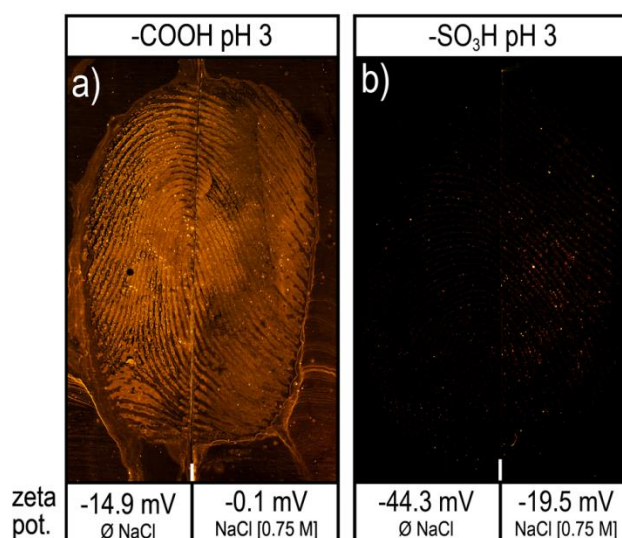
These results undermine the electrostatic interaction hypothesis. Indeed four types of NPs solutions sharing similar properties such as size and concentration have been applied onto fingerprint samples. The detection conditions (immersion time, pH) and fingerprint samples (donor, age of the marks, substrate and storage) were kept unchanged between the sets of detection. Only two parameters may have led to this absence of results:  $\zeta$  intensities and chemical groups grafted onto the NPs surface. This led us to formulate two additional hypotheses: (1) the electrostatic interaction drives the detection, but a too high  $\zeta$  leads to a very stable solution, preventing the NPs from being deposited on the mark, (2) a chemical reaction between carboxyl functions and fingerprint secretions enables the

detection. A joint effect of both  $\zeta$  and chemical groups may also be envisaged.

### *3.3. Questioning the electrostatic hypothesis*

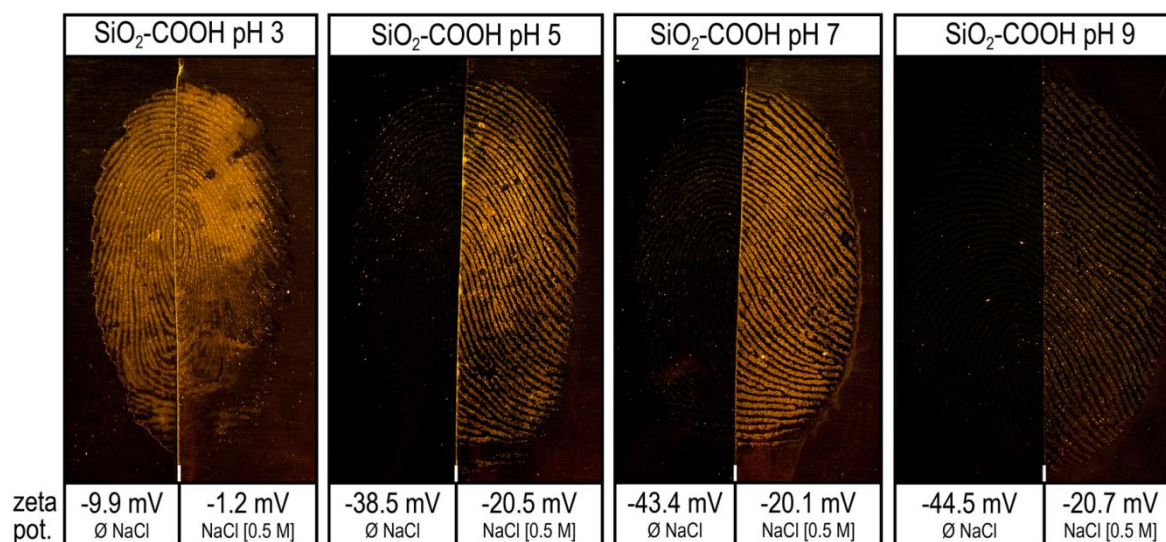
The above results indicate that detection occurs with  $\text{SiO}_2\text{-COOH}$  and  $\text{SiO}_2\text{-(COOH)}_2$ , with values of  $\zeta$  ranging from -25 mV to -15 mV. These values do not seem to affect the interaction between NPs and secretions. However, pH and  $\zeta$  remain closely related parameters that should be studied separately, in order to isolate their respective impact on the detection mechanism. Another set of experiments consist of modifying the ionic strength of the solution by adding sodium chloride (NaCl) to the NPs solution. The aim is to influence the  $\zeta$  without altering the pH of the solution.

Measurements made on  $\text{SiO}_2\text{-COOH}$  and  $\text{SiO}_2\text{-SO}_3\text{H}$  NPs solutions show that addition of NaCl lead to a decrease of  $\zeta$  intensity proportional to the amount of NaCl added, but independently of the pH of the solution. The effect of  $\zeta$  on fingermark detection ability is then studied. For both functionalizations, a solution without NaCl is also applied as for comparison purposes (figure 9). The results obtained with  $\text{SiO}_2\text{-COOH}$  firstly indicate that the presence of NaCl in the solution does not hinder the detection of fingermarks (figure 9a), with successful mark detection even at low  $\zeta$ . However, the application of solutions containing NaCl led to marks of lower quality compared to those obtained with the solution without NaCl. This is due to the fact that at pH 3 and with such salt concentration, the  $\zeta$  of the particles is close to zero and is therefore not sufficient to ensure a proper stability of the NPs in solution. When it comes to  $\text{SiO}_2\text{-SO}_3\text{H}$  NPs, even with low  $\zeta$ , no marks could be detected (or to a very limited extend in comparison to the results obtained with the carboxylic group) (figure 9b). These results clearly indicate that the  $\zeta$  of NPs is not the main criterion influencing the interaction, hence confirming that electrostatic interaction is not so critical in the detection process.



**Figure 9.** Results obtained after application of SiO<sub>2</sub> NPs functionalized with: a) carboxyl groups, b) sulfonate groups, at pH 3. Solutions containing sodium chloride [0.75M] are applied on the right side of the marks.

To evaluate the influence of the pH, SiO<sub>2</sub>-COOH NPs are applied at pH 9, 7, 5 and 3, with and without NaCl in the solution (figure 10). These results provide another important element to the understanding of the underpinning mechanism. For a standard solution of SiO<sub>2</sub>-COOH, detection of fingerprints occurs only if the pH is adjusted around 3 and if the  $\zeta$  is located between -25 and -15 mV. When NaCl is present in the solution, fingerprints can be detected at pH above 3 up to pH 7. Indeed, at pH 5 and 7, NaCl reduces the  $\zeta$  at about -20 mV. At pH 9,  $\zeta$  is also in the range of -20 mV, but the detection obtained is not as satisfactory as the previous ones. This indicates that pH affects the detection mechanism but only to a limited extent. At basic pH range, for  $\zeta$  of -40 mV, the detection does not occur. Moreover, the assumption that fingerprint residue is positively or negatively charged depending on the pH of the solution could not be verified here since negatively charged NPs interact with a supposed negatively charged fingerprint at basic pH range.



**Figure 10.** Results obtained after application of SiO<sub>2</sub> NPs functionalized with carboxyl groups, at pH varying from 3 to 9. The fingerprint samples are deposited on aluminum foil. The right half of the marks is treated with the solution containing sodium chloride [0.5M].

It can be inferred from these results that an interaction between NPs and fingerprints occurs only when a carboxyl group is present on the NPs surface. No detection takes place in absence of these groups, regardless of the pH. This goes in favour of a chemically driven detection process. However,  $\zeta$  still remains a parameter to be taken into account. Indeed, even if carboxyl groups are present, too a high  $\zeta$  hinders the detection by keeping the NPs in solution. The chemical interaction hypothesis is consequently explored further below.

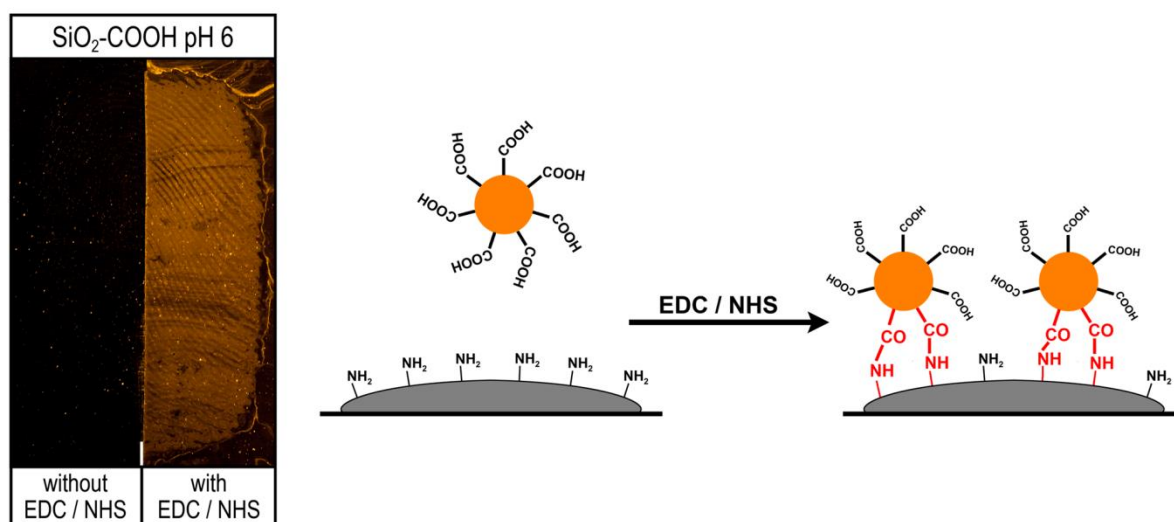
### 3.4. Exploring the chemical interaction hypothesis

Results obtained so far indicate that carboxyl groups are involved in the detection process. They can reasonably be expected to form a peptide bond with the amine groups present in the secretions. This hypothesis is justified by the presence of both amine and carboxyl groups in the fingerprint secretions (e.g. amino acids, proteins). If this bond is actually created, it may be possible to promote or accelerate its creation using a coupling agent. The most popular way to promote the formation of amide linkage between carboxyl and amine groups is by using carbodiimide groups (*N*-ethyl-*N'*-(3-dimethylaminopropyl) carbodiimide hydrochloride – EDC) combined with *N*-hydroxysuccinimide (NHS) [32]. Together they activate carboxyl groups that will readily react with primary amines.

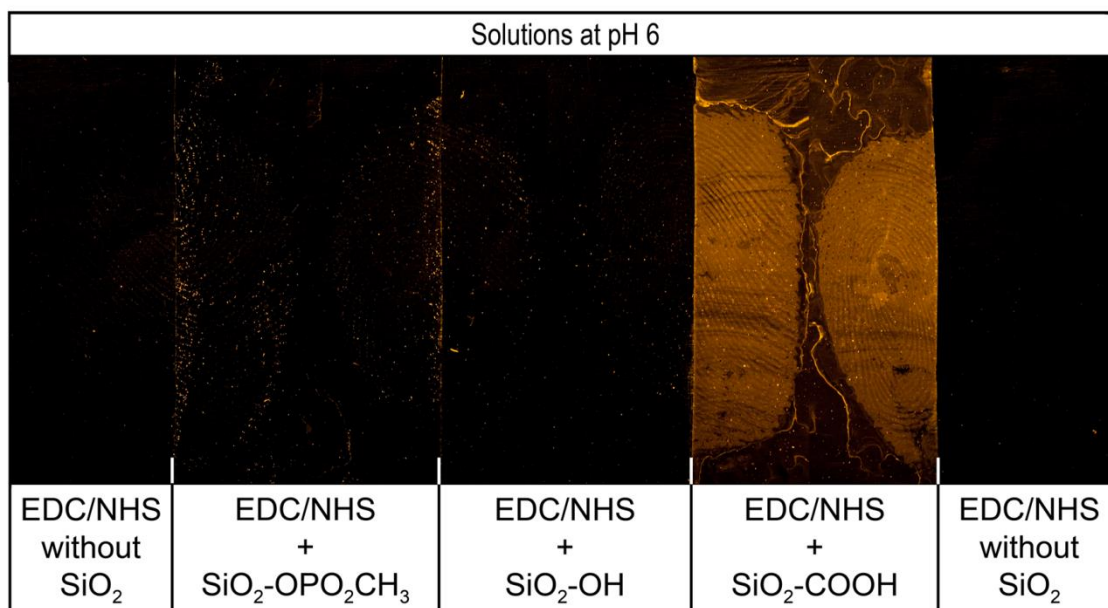


Figure 11 illustrates a mark detected following immersion into a carboxyl-activated solution (right half) and a solution without EDC/NHS (left half), both at pH 6. For the same immersion time, the right half fingermark is detected with the activated NPs, while no counterpart is obtained in the absence of EDC/NHS.

To further verify that the reaction effectively occurs with activated carboxyl groups present on the surface of NPs, fingermarks have been immersed in three other solutions (all with EDC/NHS and at pH 6), respectively (1) without SiO<sub>2</sub> NPs, (2) with non-functionalized NPs and (3) with methylphosphonate-functionalized NPs. The results illustrated in figure 12 show that the reaction takes place only when carboxyl groups are present in conjunction with EDC/NHS.

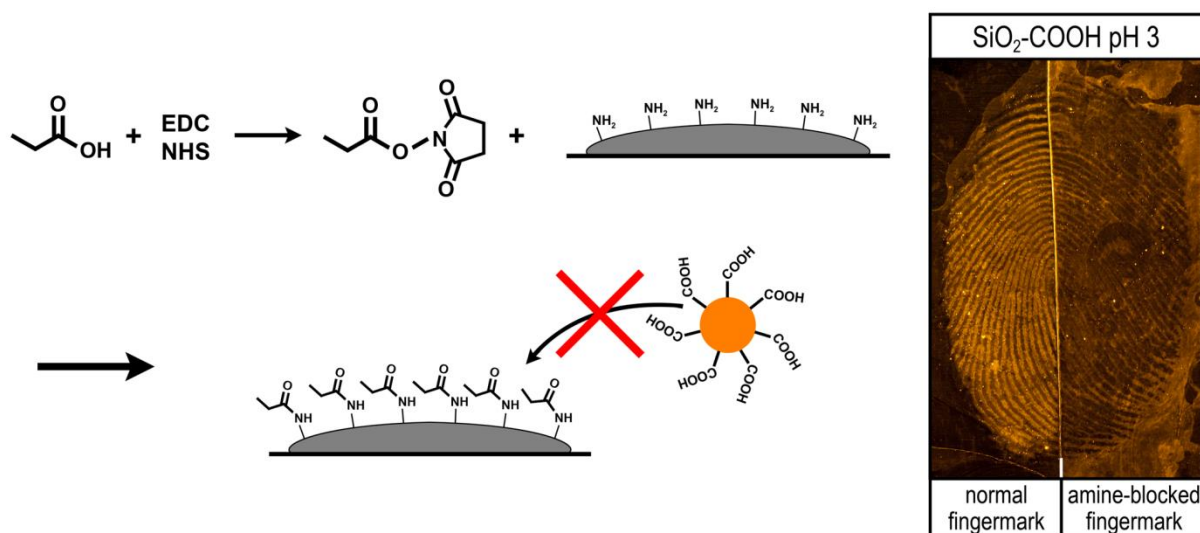


**Figure 11.** Results obtained after application of SiO<sub>2</sub>-COOH NPs at pH 6. For the right half, EDC/NHS is used to mediate the reaction. On the right is a schematic illustration of the bond formation between carboxyl groups present on SiO<sub>2</sub> NPs surface and amine groups found in the fingerprint secretion. The amide linkage is mediated by the use of EDC/NHS.



**Figure 12.** Illustration of the influence of the carboxyl groups at the NPs surface. Only solutions containing NPs functionalized with carboxyl groups are interacting with the marks.

Furthermore if the amine groups present in the residue are involved in the reaction process, it should be possible to hinder the bond formation by making them unavailable for the reaction with SiO<sub>2</sub>-COOH NPs. To do so, a propionic acid solution is activated using EDC/NHS and fingerprints are first immersed in this “amine-blocking” solution. Samples are then rinsed to remove the unreacted compounds, and immersed in a SiO<sub>2</sub>-COOH NPs solution at pH 3. The image shown in figure 13 illustrates the effect of the “amine-blocking”; pretreated half fingerprints do not react with the SiO<sub>2</sub>-COOH NPs and the fingerprint ridges are not detected, while non-blocked marks react normally. This result indicates that amine groups in the fingerprint residue take effectively part in the detection process.



**Figure 13.** Result obtained after application of SiO<sub>2</sub> NPs on fingerprints deposited on aluminum foil, at pH 3. The right half has previously been treated with an “amine-blocking” solution. On the left is a schematic illustration of the “amine-blocking”, which hinders the bond formation between carboxylic groups present on SiO<sub>2</sub> NPs surface and amine groups found in the fingerprint secretion.

#### 4. Conclusion

Functionalized silicon oxide nanoparticles (SiO<sub>2</sub> NPs) in aqueous solution have been used to study the mechanisms at play during the detection of fingerprints with the multimetal deposition technique (MMD, based on colloidal gold). The commonly accepted hypothesis for the detection mechanism is that of an electrostatic interaction, taking place in acidic conditions, between the negatively charged gold NPs and the positively charged fingerprint residue. This paper provides evidence to refute that hypothesis and suggests a more probable path in the form of a chemical reaction between carboxylic groups of the NPs and the amines contained in fingerprint residue.

These results provide new insights into the fundamental principles involved in fingerprint detection using NPs. Such understanding gives promising routes to be applied to other detection techniques based on NPs such as the silver-based physical developer [33] which still relies on unverified hypotheses.

**Author contribution**

The concept of the study and experimental design was agreed between all authors. The experimental work was carried out by SM. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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