Gold Nanoparticles

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Visualization of Latent Fingermarks by Nanotechnology: Reversed Development on Paper—A Remedy to the Variation in Sweat Composition**

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Paper is one of the most frequently tested surfaces for the detection of latent fingermarks in criminal and terrorist-related investigations. Despite the plethora of modern physical and chemical fingerprint-detection techniques,[1] a considerable portion of the latent fingermarks still escape detection. A plausible explanation is the remarkable difference in sweat composition between individual persons.[2] A potential remedy to this problem could be achieved by reversing the roles, that is, developing a fingerprint-detection technique in which paper serves as the substrate for the interaction with the reagent, while the latent fingermarks will serve as a mask.

In this work, "negative" fingermarks have been developed on paper, even after soaking in water, by the application of a new bifunctional reagent attached to gold nanoparticles (AuNPs), and then a silver physical developer (Ag-PD). The bifunctional reagent is composed of an active head, that is, a polar group with high affinity to cellulose, attached by a long chain to an active tail containing a sulfur group, which can stabilize AuNPs. Through the active head, the AuNPs, which are stabilized by the active tail, adhere preferentially to the paper cellulose rather than to the fingerprint material, to which they conventionally bind. Consequently, Ag-PD, which normally develops sebaceous fingermarks by precipitating dark silver on the sebaceous material, precipitate preferentially on the gold-coated areas giving rise to the appearance of uncoloured ridge detail on a dark background. In this competing process, the paper itself serves as the substrate, whereas the fingermarks serve as a mask. This process may increase the overall yield of developed fingermarks as it bypasses the issue of the remarkable differences in sweat composition between individual persons.

Functionalized nanoparticles have drawn great interest during the past decade not only in potential applications as biomedical, electronic, catalytic, and optical materials, but also in forensic science, as visualizing reagents for latent fingermarks.[3]

Accumulative results on a large number of paper items such as used checks, all of which are supposed to bear latent fingemarks, have shown that over 50% escape detection of identifiable marks.[4] Such observations have led to intensive research into more-sensitive fingerprint detection techniques. Paper that has been wetted is a particular challenge since the amino acids, which are the main substrate for chemical enhancement of latent fingermarks, are dissolved and removed by the water.

A silver physical developer (Ag-PD), comprising an aqueous solution of silver nanoparticles (AgNPs) stabilized by cationic surfactants, is required to achieve satisfactory development of such fingermarks. Silver slowly deposits on the water-insoluble components of the sweat, forming dark grey to black impressions (Figure 1).[5] Although the technique is quite sensitive, it suffers from several inconveniences, including complexity, lack of reproducibility, solution instability, and often poor contrast.[1,3a,5,6]

Figure 1. Sebaceous fingermark developed by Ag-PD.

As a result, many forensic laboratories refrain from using this technique on a routine basis. Latent fingermark enhancement by gold nanoparticles stabilized by citrate ions in aqueous medium, and then a modified Ag-PD, is currently used in a process known as colloidal gold or multimetal deposition (MMD).[7] AuNPs adhere to the fingermark residue and catalyze the precipitation of metallic silver from the Ag-PD solution. The gold adherence to the fingermark material is explained by an ionic interaction between the negatively charged gold colloids and the positively charged components of the fingermark residue at low pH.[7] In a modification known as SMD (single-metal deposition), the enhancement of gold colloids by precipitation of silver, was replaced by gold-based growth of the nanoparticles.[7a] Several other fingerprint techniques that are also based on nanochemical processes, have been suggested recently; all of these suggestions involve the adherence of nanoparticles to the fingerprint material.[1,3,8]

Previously we showed that good quality fingermarks were developed by treatment with an organic solution of hydrophobic AuNPs stabilized by long chain thiols, and then with

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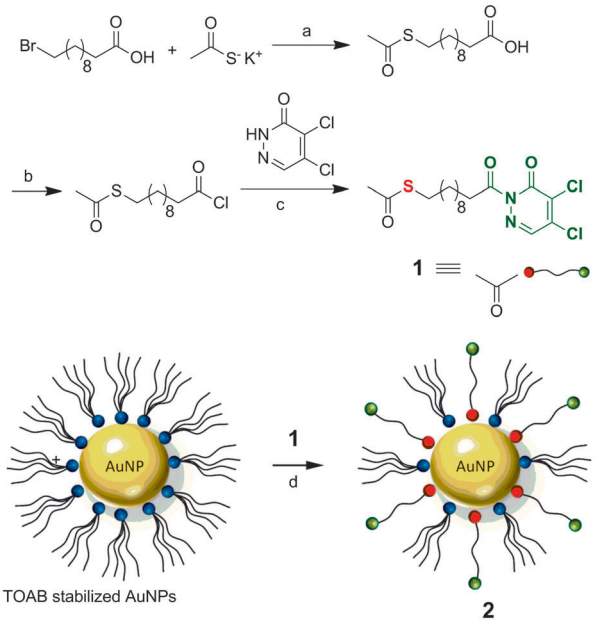
Ag-PD.[3b] The fingerprint ridge details appear as dark impressions on a light background owing to the catalytic precipitation of silver onto the gold. Like the Ag-PD and MMD techniques, however, this process too suffered from similar inconsistency, which can be at least be partially ascribed to the great variability in fingerprint residue composition.[2] As papers are composed of cellulose fibres, a method based on AuNPs–cellulose interactions should be highly versatile and reproducible. This approach requires bifunctional reagents, whose molecules contain active heads that have a high affinity to the paper, and active tails that can bind to the metallic nanoparticles. We prepared the bifunctional compound **1**, which was attached to AuNPs to form **2** (Scheme 1). Preferential binding of the AuNPs **2** to the paper was achieved through the active head, an acyl pyridazine, at the other end of the alkyl chain.



Scheme 1. Synthesis of **1** and **2**. a) CH_3CN, 85 °C, 18 h, N_2. b) CH_2Cl_2, $SOCl_2$, reflux. c) CH_2Cl_2, RT. d) Toluene, 24 h stirring, RT. TOAB = tetraoctylammonium bromide.

The AuNPs were efficiently adsorbed onto the entire paper surface (invisible to the naked eye), however, leaving the sebaceous ridges uncoated (Figure 2). A secondary treatment with conventional Ag-PD (see the Supporting Information for details) caused the precipitation of black silver on the gold-coated regions, but the sebaceous ridges remained uncoloured. Thus, the outcome of the entire process was uncoloured fingermarks on a dark background, thus having a reversed or negative appearance.

The process is fast; optimal development was usually obtained after 5 min of treatment with **2**, followed by 40–60 s treatment with Ag-PD (Figure 3). If the exhibits are left in the Ag-PD solution for a longer period of time, silver will precipitate eventually on the ridges as well, thus reducing the contrast (Figure 4). This phenomenom is explained by the occurrence of the regular Ag-PD reaction, in which the

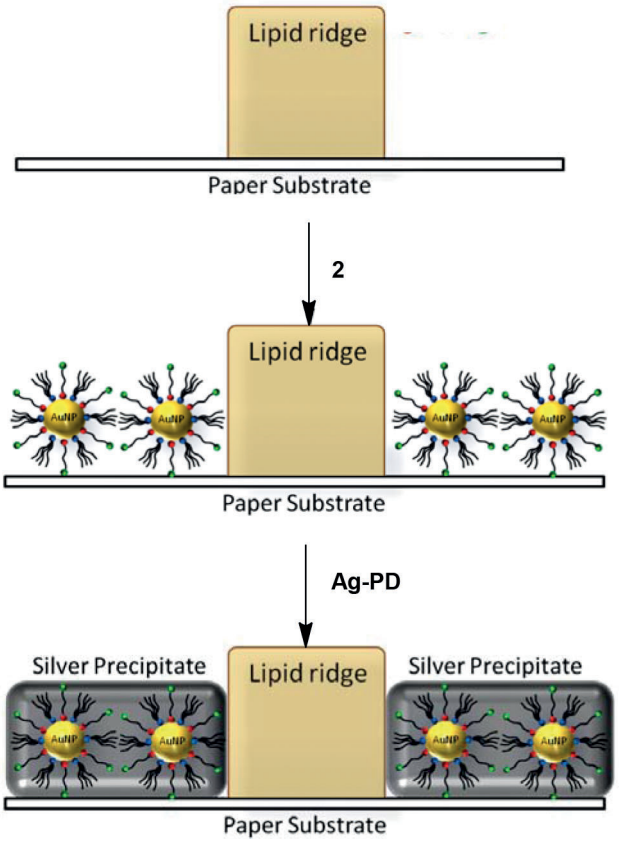


Figure 2. Latent fingermark development by treatment with **2**, followed by Ag-PD.

Figure 3. A fresh sebaceous fingermark (after soaking in water for 5 min and drying under air) developed by treatment with **2**, followed by Ag-PD.

AgNPs, which are stabilized by cationic surfactants, are stripped by the lipid fraction of the fingermarks, thus resulting in the precipitation of black silver on the fingermarks.[5b] This process apparently is much slower than the catalytic precipitation by AuNPs, and enables us to achieve a reverse development with good contrast. Working conditions are currently being optimized in regards to concentrations, immersion periods, and type of paper, as well as further modification of the ligand.

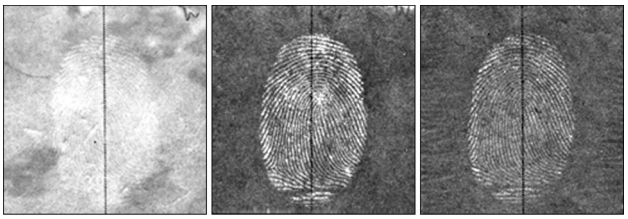


Figure 4. Fresh sebaceous fingermarks (soaked in water for 5 min and dried under air) developed by treatment with **2**, followed by immersion in Ag-PD solution for various periods of time.

Fingermarks containing relatively little tallow also developed well. Eccrine fingermarks however, could not be visualized by this technique, and gave rise to total darkening of the paper. We assume that pure eccrine material does not form an efficient mask and therefore does not prevent the active heads from binding to the paper.

The mechanism of the immobilization of **2** on paper surface is most likely hydrogen bonding between the active head and cellulose. To support (or refute) the hydrogen-bonding hypothesis, we carried two sets of experiments. The first set involved the synthesis and testing of AuNPs capped with bifunctional ligands. Some of the ligands had functional end groups that are known to form hydrogen bonds (glucose, acetylthioalkoxy bezaldehydes, and ω-mercaptocarboxylic acids,(should be:…carboxylic groups, respectively) having hydroxy, formyl, or carboxylic groups) and some had polar end groups that cannot participate in hydrogen bonding, for example, tetrachlorobenzene, or had no functionalized end groups at all (long chain thiols, as in Ref. [3b]). Each functionalized AuNP was tested for the visualization of sebaceous fingermarks on paper by the described technique. We found that "negative" fingermarks were developed exclusively by nanoparticles of the first group ,that is, those that could form hydrogen bonds, whereas the second group developed the common "positive" fingermarks.

The second set of experiments comprised the removal of the AuNPs from the treated paper by solvent. The efficiency of the removal was tested by subsequent dipping in Ag-PD solution. Fast darkening of the paper indicated that the removal was incomplete. We found excellent correlation with the previous set of experiments, that is, effective removal of AuNPs of the first group (containing hydrogen bonding end groups) required harsh conditions involving shaking the paper in Vortex in aqueous methanol, whereas removal of AuNPs of the second group was achieved by gentle shaking with petroleum ether.

An alternative explanation to the reversed appearance of the fingerprints could be cellulose acylation by **1**. Compounds of type **1** are known to be efficient acylating agents for amines and amino acids[9] and, as we found out, they are also efficient acylating agents for alcohols. This reaction, however, is slow and requires heat. No evidence for covalent binding of **1** to the cellulose hydroxy groups was found by XPS analysis, and no free pyridazine was found in the post-treatment solution.

Based on the similar behavior of AuNPs stabilized with the hydrogen-bonding ligands mentioned above, we suggest that the reversed appearance of the fingerprints results from interactions of the polar substituent at the other end of the thiol chain. The process is quite robust, and even partially degraded Ag-PD solutions produce good results.

Notably, the VMD (vapour metal deposition) technique also develops negative fingermarks, but on nonporous surfaces, particularly polyethylene and polypropylene. This method, which is based on vapour-phase coating with gold, and then zinc, under high vacuum, is considered the most sensitive fingerprint technique for these substances.[10]

In summary, by modifying the thiolic ligands, which stabilize the AuNPs, we were able to reverse the affinity of the AuNPs to the substrate, and hence to develop good quality negative fingermarks. The method presented here differs from existing techniques that are based on nanotechnology, by a major characteristic: the substrate for this reaction is paper itself and not the fingermarks; gold is attached preferentially to the paper and the fingermarks develop in a reversed mode, that is, the reaction occurs around the ridges and between them, but not on them. Optimization of this process is underway.

Experimental Section

Sebum-rich (sebaceous) fingermarks were obtained from several volunteers by rubbing their fingers against the forehead and stamping them onto A4 paper strips. The paper strips bearing the sebaceous prints were immersed in an acetonitrile solution of **2** containing 0.5% dimethylsulfoxide (prepared by dissolving the AuNPs in a small amount of dimethylsulfoxide and diluting with acetonitrile) for periods ranging from 10 s to 5 min, followed by development with Ag-PD. Best results were obtained by immersion in Ag-PD for approximately 50 s. Yet, the decision of when the fingerprint is sufficiently developed should be made by observation. It is important to rinse the paper in water immediately after the Ag-PD treatment.

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