Application of nanoparticles for the enhancement of latent fingerprints

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Received (in Cambridge, UK) 2nd January 2007, Accepted 5th February 2007
First published as an Advance Article on the web 19th February 2007
DOI: 10.1039/b618966k

Two different types of nanoparticles dissolved in organic solution, gold stabilized by *n*-alkanethiols and CdSe/ZnS stabilized by *n*-alkaneamine, adhere preferentially to the ridges of latent fingerprints; the gold deposits catalyze silver electroless deposition from "Silver Physical Developer" (Ag-PD), an aqueous solution containing silver colloids stabilized by cationic surfactants, to form dark impressions of the ridge details; the hydrophobic capped gold nanoparticles significantly improve the intensity and clarity of the developed prints compared with Ag-PD alone; fingermarks treated with CdSe/ZnS nanoparticles can be viewed directly, due to their fluorescence under UV illumination.

Silver physical developer (Ag-PD) is the standard reagent for developing latent fingerprints on wet, porous surfaces such as paper and cardboard. Deposition of silver on the water insoluble residues of latent fingerprints creates a black silver precipitate along the fingermark ridges. This process is based on an electroless deposition reaction, in which Fe^{2+} ions reduce the Ag^+ ions to metallic silver, a process which is presumably catalyzed by the fatty components of the fingermark material. Yet, this process suffers from the instability of the developing solution and therefore of poor reproducibility.[1,2] Latent fingerprint enhancement by gold nanoparticles stabilized by citrate ions in aqueous medium, followed by Ag-PD, is currently used in a process known as "colloidal gold" or "Multi-Metal-Deposition" (MMD).[1,3] The gold nanoparticles 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.[1,4]

Metal surfaces are known to catalyze the reduction of different metals from solution by electro and electroless deposition.[5,6] Certain metallic nanoparticles showed the same catalytic properties.[7] Aslam *et al.* showed that gold nanoparticles stabilized with dodecanethiol in organic medium are adsorbed onto activated hydrophobic surfaces by hydrophobic interactions.[8] In this work we found that fingermark deposits can serve as the hydrophobic surface for such interactions and gold nanoparticles dissolved in petroleum ether, capped with different *n*-alkanethiols, adhere preferentially to the ridges of sebum-rich latent fingerprints. In the second phase, the gold deposits catalyze silver reduction from Ag-PD solution, which precipitates as Ag^0 on the ridges, thus significantly enhancing the developed fingermarks.

Gold nanoparticles (Au-NPs) stabilized with alkanethiol chains (octadecanethiol, tetradecanethiol and decanethiol) were synthesized according to Brust *et al.*[9] TEM and nanosizer measurements showed the formation of gold spherical particles with an average size of 2–3 nm. They are much smaller than the gold particles in the modified MMD process, whose average size is 14 nm.[10]

Sebum-rich (sebaceous) fingermarks were obtained from several volunteers by rubbing their fingers against the forehead and stamping them onto A4 paper strips, then water soaked and dried.

The paper strips bearing the sebaceous prints were immersed in a petroleum ether solution of Au-NPs stabilized with octadecanethiol (Au-NPs-C_{18}) in different concentrations, for periods varying from 10 s to 5 min, followed by development with Ag-PD (UK PSDB formulation).[11] Best results were obtained in a 0.04% (w/v) solution and immersion time of 3 min. Shorter immersion times produced weaker prints. As a rule, the Au-NPs-C_{18} pretreatment produced clearer impressions, which developed faster (1–2 min) compared to the samples that had not been pre-treated (10–15 min). A higher background also developed, but it did not affect the quality of the prints (Fig. 1). Rinsing the paper with petroleum ether after the immersion in Au-NP solution did not reduce the background significantly, but slightly stronger prints were obtained.

On nonporous surfaces such as silicon, glass and polyethylene, high-quality prints were developed by the two-step process, while Ag-PD alone produced only poor impressions. The adsorption of Au-NPs-C_{18} on fingermarks was studied by optical microscopy and by scanning electron microscopy (SEM). Sebaceous fingermarks were impressed on silicon wafers and immersed for 3 min in a 0.04% Au-NPs-C_{18} solution. Au-NPs adsorbed preferentially

Fig. 1 Comparison between two halves of a sebaceous fingermark on paper, developed by Ag-PD (top), and by Au-NP-C_{18} followed by Ag-PD (bottom).

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onto the fingermark ridges and a very thin layer was noticed in the valleys between the ridges (also seen by energy dispersive X-ray spectroscopy (EDS) and by back scattering imaging). The nanoparticles aggregate on the fingermark ridges producing large clusters, probably due to interactions between the Au-NPs-C_{18} and the fatty residues of the latent prints as shown by Aslam *et al.*[8]

Silicon wafers on which sebaceous fingermarks were impressed were immersed in Au-NPs-C_{18} solution followed by immersion in the Ag-PD solution for periods from 10 to 90 s. SEM images showed that after 10 s heavy deposits of silver start appearing and after 60 s the ridges were almost fully coated, with only little silver in the valleys.

The precipitate had the morphology of intertwined plates, probably due to the fast growth of the deposits. EDS imaging showed that the gold aggregates on the fingermark ridges were coated with silver, while only very little silver was noticed between the ridges. Almost no deposition of silver occurred on fingermarks that had not been pre-treated with Au-NPs-C_{18}.

To test the relationship between the thiol chain length and fingermark enhancement, Au-NPs stabilized with tetradecanethiol (Au-NPs-C_{14}) and with decanethiol (Au-NPs-C_{10}) were also synthesized and compared to Au-NPs-C_{18}. Sebaceous fingermarks on paper strips were immersed in the different Au-NPs solutions, followed by Ag-PD development. Octadecanethiol and tetradecanethiol stabilized Au-NPs had a positive effect on fingermark development as compared with Ag-PD alone, while decanethiol stabilized Au-NPs gave poorer resolution and higher background compared to the untreated samples. SEM images of silicon surfaces bearing sebaceous fingermarks that had been treated with the different Au-NPs showed the following order of aggregation: $C_{18} > C_{14} > C_{10}$. This may explain the better development with Au-NPs-C_{18}. The silicon wafers were immersed in PD solution for 60 s and SEM images showed that the deposition, in the case of Au-NPs-C_{14}, was not as fast as in the Au-NPs-C_{18} case although it covered all the ridges (Fig. 2). Silver sphere-like deposits and some plate-like bundles were noticed, although much less than when employing Au-NPs-C_{18}. As a rule, Au-NPs-C_{10} induced much thinner silver deposits, although in some cases moderate growth of plate-like bundles occurred.

Petroleum ether solution of CdSe/ZnS nanoparticles (CdSe/ZnS-NPs) with average size of ∼3 nm, stabilized by octadecaneamine were prepared according to Peng and co-workers[12] with slight modifications (a ZnS shell instead of CdS shell) and tried as a fingermark reagent. Silicon wafers and paper strips, bearing impressed sebaceous fingermarks were immersed in a 0.04% (w/v) petroleum ether solution of CdSe/ZnS and, after drying in air observed under UV illumination. Clear fluorescent prints could be viewed on the silicon surface. Optical microscopy in UV mode showed CdSe/ZnS NPs aggregates on the fingermark ridges (Fig. 3). On paper, however, it was impossible to visualize the fingermarks due to strong background fluorescence.

This method opens a new possibility for visualizing latent fingerprints on wet non-porous surfaces without the need for using a post treatment with a PD solution.

In summary, Au-NPs stabilized by *n*-alkanethiol chains and dissolved in petroleum ether, adhere to fingermark material and enhance the development of latent fingerprints by the Ag-PD method. The metal nanoparticles presumably adsorb onto the

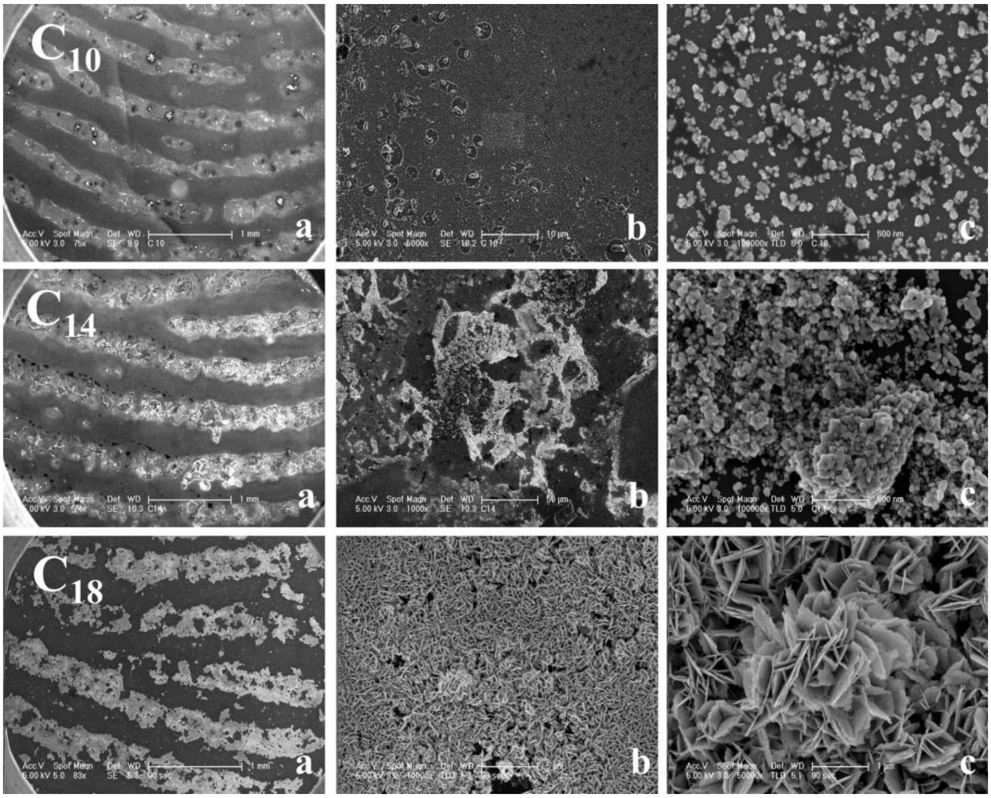

Fig. 2 SEM images of silver deposition (bright areas) on sebaceous fingermark impressed on silicon surface with different Au-NPs. Magnification: (a) 75 ×, (b) 1000–5000 ×, (c) 5000–10000 ×.

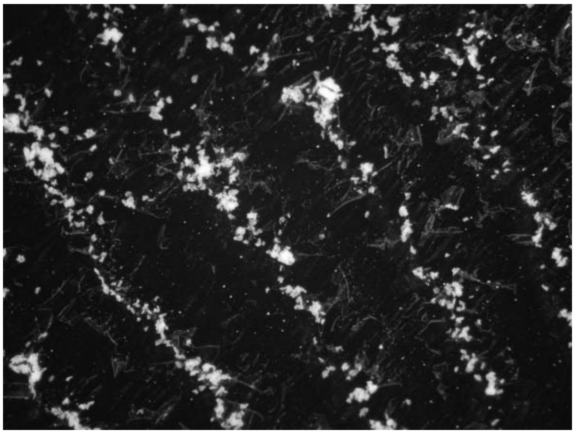

Fig. 3 Optical microscope in the UV mode image of CdSe/ZnS-NPs adsorbed preferentially on fingermark ridges on a silicon surface.

ridges by hydrophobic interactions, a totally different mechanism from the assumed ionic interaction in the "classical" MMD process. A clear relationship between the chain-length of the stabilizing thiols and the fingermark quality was found: the longer the chains, the clearer are the fingermarks.

Fluorescent CdSe/ZnS-NPs from organic solution adhere preferentially to latent fingerprints on nonporous surfaces, enabling their visualization by examination under UV illumination (see also ref. 13).

This work was supported by the Hebrew University under the Scientific Innovation project.

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