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One step to detect the latent fingermarks with gold nanoparticles

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ABSTRACT

A simple and environment friendly chemical route for detecting latent fingermarks by one-step single-metal nanoparticles deposition method (SND) was achieved successfully on several non-porous items. Gold nanoparticles (AuNPs) synthesized using sodium borohydride as reducing agent in the presence of glucose, were used as working solution for latent fingermarks detection. The SND technique just needs one step to obtain clear ridge details in a wide pH range (2.5–5.0), whereas the standard multi-metal deposition (MMD) technique requires six baths in a narrow pH range (2.5–2.8). The SND is very convenient to detect latent fingermarks in forensic scene or laboratory for forensic operators. The SND technique provided sharp and clear development of latent fingermarks, without background staining, dramatically diminished the bath steps.

1. Introduction

Hitherto, fingermarks constitute one of the most important categories of physical evidence in the forensic science. In past decades, methods of visualization of fingermarks have been developed significantly, such as iodine fuming, ninhydrin, silver nitrate [1], and cyanoacrylate fuming [2–4]. Recently, nanoparticles were widely used in this filed, e.g. CdS [5–8], CdTe [9], SiO_2 [10], and AuNPs. Multi-metal deposition method (MMD), as a useful mean to detect latent fingermarks on porous and non-porous items, was first proposed by Saunders in 1989 [11,12]. It is a two-step wet chemical process for latent fingermarks detection, combining the principles of small particles reagent with AuNPs and following a silver physical developer (AgPD). It is an equivalent, and usually superior to the well-known methods of cyanoacrylate fuming [2–4] and vacuum metal deposition [13] on various kinds of items. Schnetz and Margot used smaller AuNPs to take further studies on MMD procedure, yielding better results [14]. They explored the influence of particle size, pH value, concentration of the colloidal gold solution and the concentration of Tween 20 on detecting latent fingermarks. Mandler and Almog [15] proposed AuNPs stabilized by n-alkanethiols according to Brust et al. [16] to detect latent fingermarks on porous items in petroleum ether. Meanwhile, they probed the relationship among the thiol chain length, concentration of AuNPs, and fingermark enhancement. Becue et al. developed a new MMD technique of modifying AuNPs with mercaptocyclodextrin as a host for organic dye. This technique reduced the bath numbers and enhanced the latent fingermarks through utilizing organic dye instead of AgPD [17]. Stauffer et al. presented a single-metal deposition (SMD) to visualize latent fingermarks [18]. In the second step, they replaced the AgPD with tetrachloroauric acid and hydroxylamine hydrochloride to enhance the fingermark detection. Actually the SMD technique is quite similar to the standard MMD technique. Latent fingermarks detection techniques, as described above, suffer from restrictive experimental conditions, such as bothersome processes to prepare precursors (AuNPs), many baths, high cost preparation, and even some harmful solvents involved. So far, latent fingermarks detection only with AuNPs through one-step has not been reported yet.

AuNPs have received considerable attention for potential applications in the fields of physics, chemistry, optics, biology, electronics, and materials science [19]. A variety of methods have been reported and reviewed for preparation of AuNPs [10,20–23]. The most commonly used method is chemical reduction of gold salts by various reductants, such as sodium citrate [22], thiocyanate [20], and sodium borohydride [10]. Several forensic science laboratories [12,14–16,20] have also concluded that colloidal gold is a particularly effective reagent on detecting latent fingerprints.

In this work, glucose stabilized AuNPs were synthesized and utilized as working solution to detect latent fingermarks. Two methodologies, the SND and MMD, were applied in fingermarks detection under the same condition. The influence of pH values

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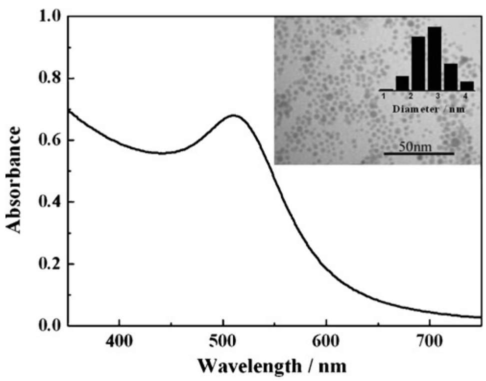

Fig. 1. UV–vis absorption spectrum, TEM image, and corresponding particle size distribution histogram (inset) of the glucose stabilized AuNPs (concentration of tetrachloroauric acid is 1.0 mM).

on detecting latent fingermarks was also explored. It was found that the SND technique provided sharp and clear development of latent fingermarks, without background staining, dramatically diminished the bath steps in a wide pH range.

2. Experimental

2.1. Chemicals

Chloroauric acid tetrahydrate, sodium borohydride, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Citric acid was purchased from Beijing Chemicals (Beijing, China). Glucose was purchased from Aldrich (USA). All of the chemical reagents were used without any further purification. All glassware used in the following procedures was cleaned in a bath of freshly prepared 3:1 HCl/HNO_3 (v/v), and rinsed thoroughly with double distilled water prior to use. All the experiments were carried out at room temperature.

2.2. Preparation of AuNPs

Glucose stabilized AuNPs were prepared according to the following procedures: 2×10^{-5} mol chloroauric acid tetrahydrate and 2×10^{-4} mol glucose were dissolved in 18 ml deioned water in a flask with stirring. 30 min later, a freshly prepared 2 ml ice-water solution of sodium borohydride (1×10^{-4} mol) was added dropwise into the above solution under vigorous stirring. Color of the solution changed immediately from straw yellow to wine red, indicating the formation of AuNPs. After stirring for 1 h, the prepared AuNPs were used for detecting latent fingermarks.

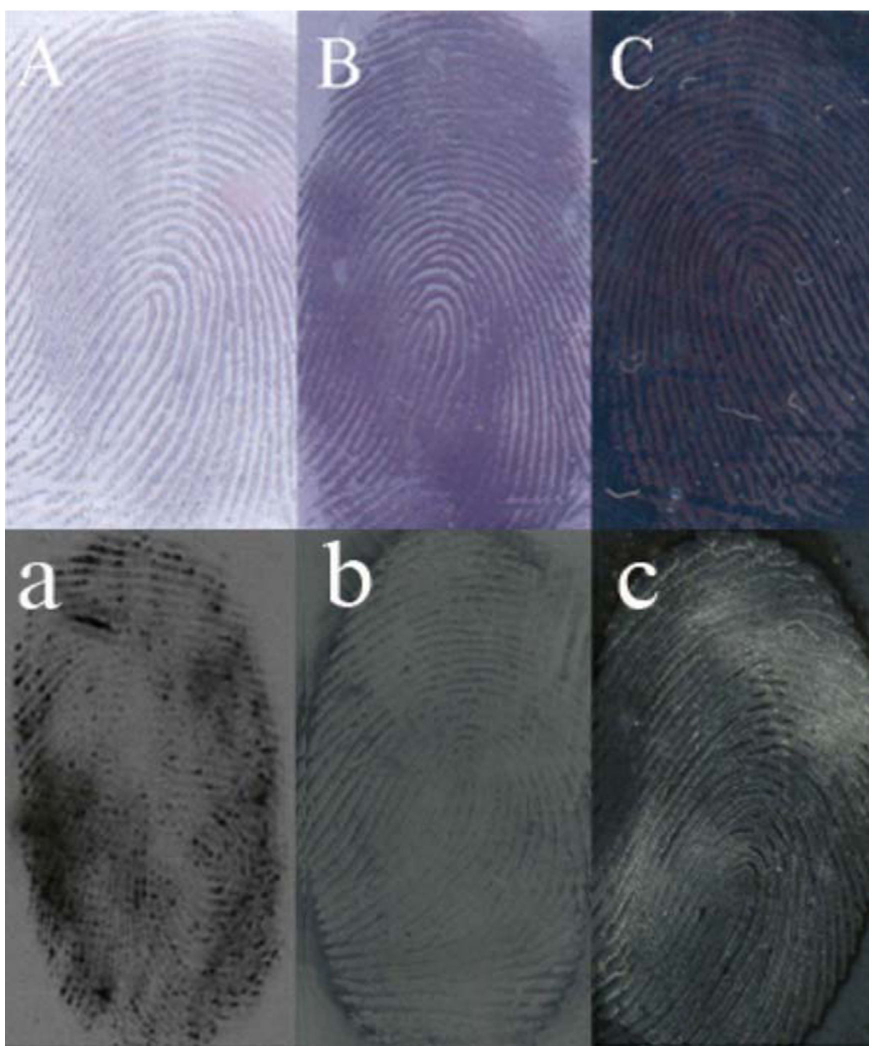

Fig. 2. Latent fingermarks were developed with the SND technique using glucose stabilized AuNPs on (A) glass slide, (B) plastic, and (C) tin foil; and with the standard MMD technique on (a) glass slide, (b) plastic, and (c) tin foil.

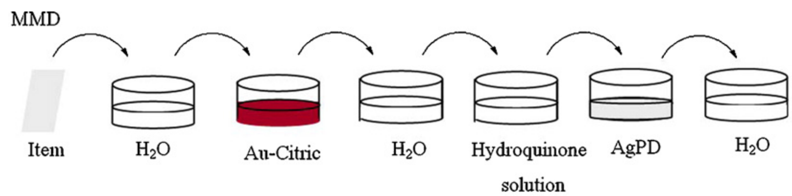

Fig. 3. Schematics of the standard MMD and the SND technique.

2.3. Detection of latent fingermarks

Latent fingermarks were obtained all from one volunteer by rubbing fingers against the forehead and stamping them onto glass slides, plastic and tinfoil at the same condition, respectively. The obtained latent fingermarks are similar to real samples on the same items.

Citric acid (1 M) and sodium hydroxide (1 M) solution were used to adjust the pH value of the prepared AuNPs. Then, the items bearing latent fingermarks were immersed into the working solution, removed from the solution 40 min later, rinsed with deioned water, and dried with nitrogen steam. Clear ridges of prints were obtained.

Control experiments were carried out at pH 2.8, using the SND and the standard MMD [14].

The influence of the pH on detecting latent fingermarks was further investigated. Different pH was adjusted with citric acid (1 M) and sodium hydroxide (1 M) (2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 5.5, 6.0, and 7.0) to detect latent fingermarks at room temperature.

2.4. Instrumentations

UV–vis measurement was carried out on a Cary 50 UV–vis spectrophotometer (Varian, USA). TEM measurement was performed on a JEOL 2010 transmission microscopy operated at an accelerating

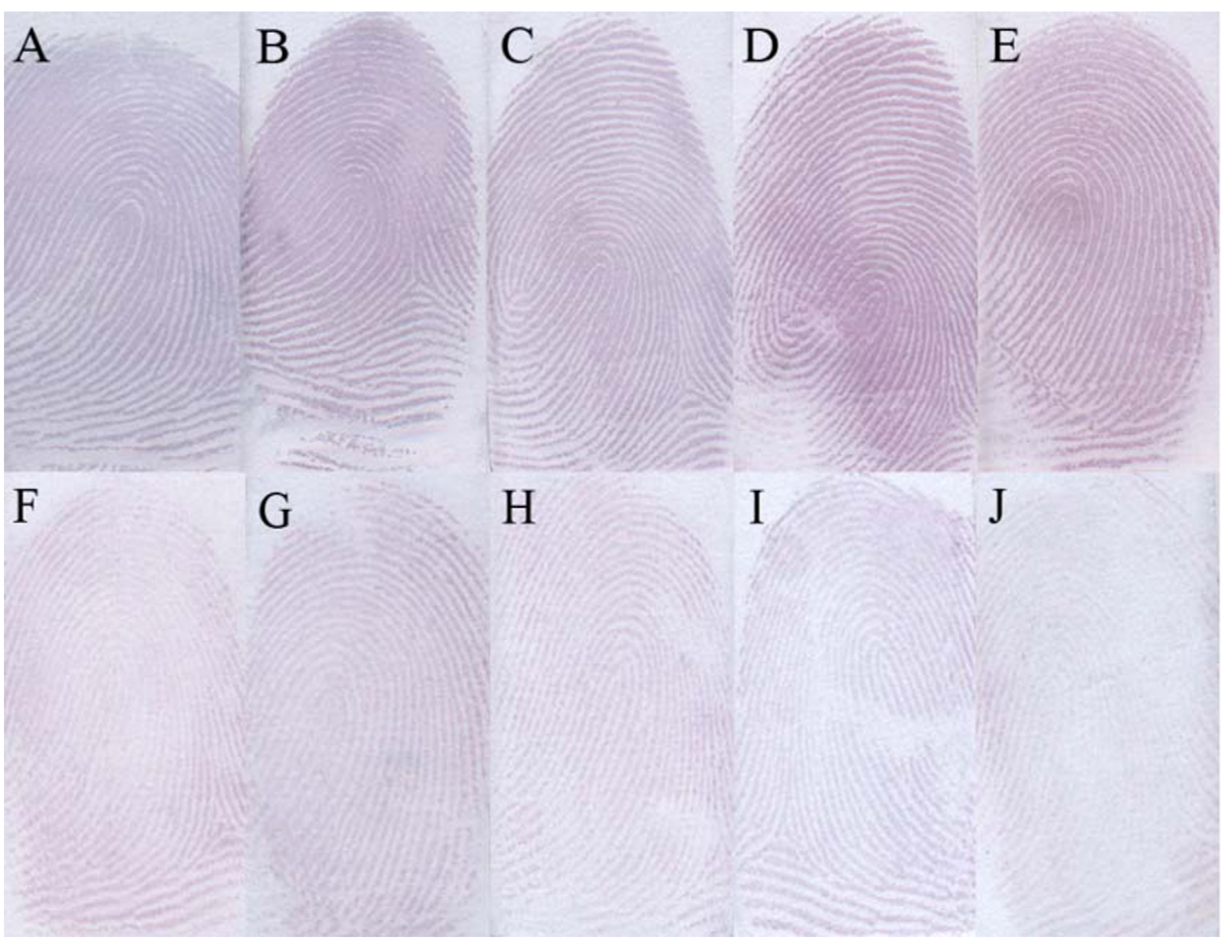

Fig. 4. The pH influence of colloidal gold solution on the fingermarks detection on glass slides: (A) 2.0, (B) 2.5, (C) 3.0, (D) 3.5, (E) 4.0, (F) 4.5, (G) 5.0, (H) 5.5, (I) 6.0, and (J) 7.0, respectively.

voltage of 200 kV. The sample for TEM measurement was prepared by placing a drop of as-prepared AuNPs solution onto a carbon-coated copper grid and dried at room temperature. SEM and EDAX measurement was taken on a FE-SEM, S-4800, Hitachi Scanning Electron Microscopy. Photos were taken with Nikon D100 made by Nikon Corporation.

3. Results and discussion

AuNPs were prepared using sodium borohydride as the reducing agent in the presence of glucose. The UV–vis spectrum and TEM image were used to confirm the formation of AuNPs (Fig. 1). The UV–vis spectrum of the AuNPs shows an absorption peak at 511 nm, assigned to the characteristic surface plasmon resonance [19]. TEM image was applied to further confirm the AuNPs formation. Inset of Fig. 1 displays the AuNPs are generally well-separated from each other. The size distribution histogram shown in the inset reveals an average diameter of 2.5 nm, as judged from more than 200 individual particles, which is much smaller than particles in Schnetz and Margot's work (14 nm).

Control experiments were carried out between the SND and the standard MMD technique. The items bearing latent fingermarks were immersed into the glucose stabilized AuNPs at pH 2.8 for 40 min, and washed with deioned water to remove redundant AuNPs, natural drying. On glass slide, plastic and tinfoil, high quality prints were developed and shown in Fig. 2A–C. Meanwhile, control experiments were carried out according to the MMD procedure [14]. Correspondingly, Fig. 2a, b, and c were the results developed on glass slide, plastic, and tin foil, at the same condition as above. Comparatively, both of the two methods can obtain quasi-identical ridge details of fingermarks. Nevertheless, the SND procedure has no background interference and shows much clearer ridge details than the MMD procedure (Fig. 2). The color of fingermarks detected by the SND is reddish while the other is black with MMD procedure.

The standard MMD and the SND technique procedures were schematically depicted in Fig. 3. The standard MMD is seldom used in forensic laboratories, due to its labor intensive, time consuming, and only producing dark grey or black fingermarks. The MMD laboratory procedures are consisted of six consecutive baths into which the items were immersed for different time (upper in Fig. 3). The first three baths assure the deposition of gold colloids, while the other three baths were the reduction of silver on the gold colloids to enhance the detected latent fingermarks to be grey or black. The SND technique was carried out in two baths, with no reinforcing reagent (as AgPD or organic dye) just glucose stabilized AuNPs (lower in Fig. 3). The SND has significantly diminished the number of laboratory operations, and cut the cost for detecting latent fingermarks. So the procedure might be an attractive alternative to the MMD procedure.

The influence of pH on detecting fingermarks was further explored. Latent fingermarks were immersed in different pH solutions of glucose stabilized AuNPs (2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 5.5, 6.0, and 7.0) for 40 min, washed with deioned water, and dried with nitrogen steam (as shown in Fig. 4). In a wide pH range, marks on glass surfaces could be visualized well. At a low pH value, the synthesized AuNPs are unstable and aggregated easily, so the fingermarks are light blue (Fig. 4A and B). At high pH value, there are not enough protons to activate the protein or peptide included in the latent fingermarks. So the obtained results are not as good as those in lower pH solution. In the neutral condition (pH 7.0), there were almost no ridge details obtained. From these points we conclude that the favorable pH range for latent fingermarks detection is around 2.5–5.0, which is obviously wider than traditional MMD (only working for pH 2.5–2.8). It is much convenient for workers to detect latent fingermarks in forensic science or laboratory.

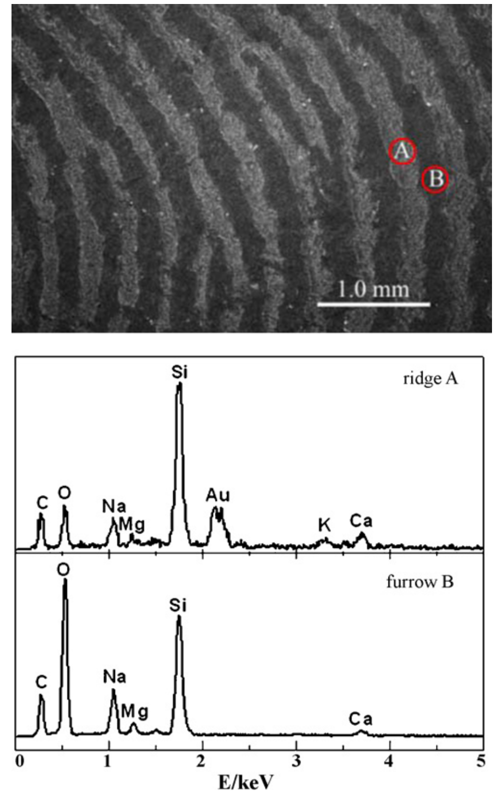

Fig. 5. SEM image of detected fingermarks with glucose stabilized AuNPs on silicon wafer and EDAX analysis for the ridges (region A in SEM image) and furrows (region B).

The binding mode of the AuNPs to the fingermark residues remains misunderstood, even if the electrostatic attraction is the most widely accepted one. The theory is that proteins or amino acid containing components within a fingermark can be protonated under acidic conditions and thus charged positively. Negatively charged AuNPs are deposited preferentially onto the fingermark ridges through electrostatic interactions or non-covalent interaction [6]. There are more components, like oil, protein and salt, on the ridges of the fingermarks than on the furrows [7]. So there are more AuNPs attracted on the ridges. Hence, latent fingermarks can be revealed. Fingermarks detected by glucose stabilized AuNPs on silicon wafer was characterized by SEM and EDAX (Fig. 5). Au element appeared on the ridges of the developed latent fingermarks (Fig. 5 ridge A), while no Au element on the furrows (Fig. 5 furrow B).

4. Conclusion

In this report, a one-step single-metal nanoparticles deposition method (SND) has been proposed for detecting latent fingermarks on non-porous items. AuNPs stabilized by glucose have been successfully synthesized and suggested to be utilized as the working solution to detect latent fingermarks. The SND technique could obtain even better results in a wide pH range compared with the standard MMD. It is a simple method to detect latent fingermarks only with AuNPs and just in one step rather than tow or more. This technique has dramatically diminished the baths, operated simply and expediently, and enlarged the pH range for detecting latent fingermarks. These may establish a new possibility for the detection of latent fingermarks in forensic science.

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