Spontaneous redox route for gold-aryl film development of latent fingerprints on nickel coins

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Abstract

Surface modifiers through redox routes emerged as the most preferred in forensic science. Aryldiazonium salts stabilized with tetrachloroaurate(III) are excellent redox modifiers in the development of latent fingerprints on nickel surfaces. Nickel coins were fingerprinted and developed with a stable diazonium salt $[\text{O}_2\text{N}-4-\text{C}_6\text{H}_4\text{N}\equiv\text{N}]\text{AuCl}_4$. The developed surfaces were studied using XPS which showed the presence of the characteristic gold and organic modifier peaks. In addition, imaging analysis using SEM showed clusters of gold. EDS quantitative analysis estimated a good amount of gold presence on the fingerprinted compared to the non-fingerprinted area. Our results are important in the analysis of nickel coins using a spontaneous route by simply depositing diazonium salt solution drops on the nickel surface without any additional reducing agent. This work brings strong supporting evidence for the efficient combination of diazonium surface chemistry and high-performance surface analytical tools (XPS, SEM-EDS) in the fast, spontaneous developing of fingerprints and their morphological and chemical composition assessments.

Keywords. Forensics, Diazonium Gold Salt, Nickel Coins, XPS, Latent Fingerprints, Gold-Aryl Film.

1. Introduction

Redox approaches in forensic science investigation emerged as the preferred choice for surface chemists.¹⁻³ Reducible gold(III) precursors stabilized with an organic moiety such as diazonium have been stabilized and developed in forensic science to be handled at ambient conditions.⁴ Their enhanced solubility made them the first choice in developing metals and nonmetals. They are prone to spontaneous redox reactions without the need for electrochemical or chemical stimuli. They also form robust metal-carbon bonding which persists under environmental conditions.⁵⁻¹⁰ Recently, we investigated aryldiazonium tetrachloroaurate(III) salts as developers for latent fingerprints collected on several metals such as aluminum, lead and copper.¹¹ Compiled data suggested that the salts are excellent modifiers on copper surfaces but no other metals due to their high reduction ability which resulted in poor quality development over all fingerprint. The cleavage of molecular nitrogen as bubbles and the immediate development can be seen. XPS study on copper surfaces resulted in the formation of gold(0) accompanied by copper oxide formation.¹¹

Nickel-diazonium interface has been of central interest to investigate which can spontaneously reduce the diazonium salts by just simple dipping, induction heating or electrochemical reduction with low oxidation potential (-0.257 V vs. SHE).^{6,13-15} The resulting attached organic layer shows high stability and resistance of sustained ultrasonic rinsing in different solvents.⁷

Nickel-plated brass is one of the major types of casings encountered in the market cartridge casing.^{16,17} It was used primarily as a method of preventing the verdigris and corrosion to brass ammunition stored in leather cartridge belts and bags. In coins, nickel alloys were used in many countries and regions worldwide such the United States,¹⁸ UK coins,¹⁹ Euro, and Sweden.²⁰

Nickel has been investigated in forensic science in counterfeit watches and coins,²¹⁻²³ human teeth involved crimes,²⁴ illicit cocaine,²⁵ prints on cartridge casings and shotgun shells²⁶ and cosmetic evidence.²⁷ Several techniques were used in the analysis such as XPS, XRF, XRD, ICP-MS and simple chemical modification.^{22,25,28-34}

Herein, we bridge the gap between previous works on diazonium modification of copper and our approach applying diazonium gold to surfaces and their analyses by XPS to tackle the latent fingerprint development on nickel coins. We describe our results of spontaneous redox development of nickel surfaces using nitrobenzenediazonium tetrachloroaurate(III) (NBD AuCl₄) and studied using XPS, SEM and EDX. Nickel surfaces are more reducing than copper for example and expected to reduce diazonium salts faster and more efficiently; this is what motivated our choice of one French Franc nickel coin to conduct the study within the framework of forensic surface chemistry and surface analysis.

2. Materials and methods

2.1. Instruments

A K Alpha XPS apparatus (Thermo Scientific) was used to record the spectra. The machine is fitted with a monochromatic Al K α X-ray source (spot size: 100 μ m). The pass energy was set to 80 and 200 eV for the narrow regions and survey spectra, respectively. Electron and argon flood guns were used to compensate for the static charge buildup. It is to note that charge neutralization was not necessary for cleaned nickel coin; but was applied in order to have similar analysis conditions for metal surface and the same after reaction with diazonium salt which reacts with- and acrylates the surface in addition to the deposition of gold. Metallic state nickel Ni2p_{3/2} peak was found at 852.9 eV which is the value reported in NIST database for conductive nickel surface (<https://srdata.nist.gov/xps/XPSDetailPage.aspx?AllDataNo=26452>); in this case

no further calibration was needed. For coated surfaces, gold Au4f_{7/2} peak was found at 84±0.1

eV. The composition was determined using the manufacturer sensitivity factors. SEM investigations were performed using a Carl Zeiss MERLIN field emission-scanning electron microscope (FE-SEM). In order to reveal alternating section in composition of the surface, backscattered electrons (BSE) were collected and imaged. Energy dispersive X-ray analysis (EDS) were performed using a X-Max silicon drift detector from Oxford Instruments coupled with AZtec operating system.

2.2. NO₂-aryldiazonium-AuCl₄ on glass slides

Surface preparation. Glass slides were cut into five pieces and prepared by cleaning with HCl solution to remove metal-based contamination, as well as NaOH to remove organic contaminants, then absolute ethanol.

Developing latent fingerprint on non-metal surface. The following samples were prepared for XPS analysis: Glass (clean); Glass + Fingerprint. The aryldiazonium AuCl₄ solution (0.001M) was dropped using a dropper on each of the prepared surfaces: Glass (2 h); Glass + Fingerprint (1 h); Glass + Fingerprint (2 h). The surfaces were then washed gently with deionized water until the excess salt was completely washed away and dried.

2.3. NO₂-aryldiazonium-AuCl₄ on nickel coins

Surface preparation. Nickel coins (French Franc) were prepared by cleaning with distilled white vinegar and table salt to remove the oxides, sonification to remove any dirt, then absolute ethanol.

Developing latent fingerprint on metal surface. The following samples were prepared for XPS analysis: One French Franc nickel coin (clean). The aryldiazonium AuCl₄ solution

(0.001M) was dropped using a dropper on each of the prepared surfaces: Nickel coin (1 h); Nickel coin + Fingerprint (1 h). The surfaces were then washed gently with deionized water until the excess salt was completely washed away and dried. The samples formed a film just enough to cover the suspected area.

3. Results and Discussion

The demonstration of latent fingerprints on glass slides were tested as representative materials of windows and glass bottles. However, no conclusive results were obtained after 2 h of interactions between diazonium salt solution drops and glass samples with fingerprints (no visible fingerprints were noted). This is probably due to the lack of non-reducing nature of glass. It is to note that in this work, we have used a minimum set of compounds; we simply deposited diazonium salt solution drops on the surface without any additional reducing agent. This might be the reason latent fingerprint could possibly be demonstrated on glass, via a spontaneous redox process. Indeed, it was reasonable to expect possible reaction between diazonium group and silanol groups resulting in Si-O-N=N-aryl interface.

Samples consisted of clean nickel coin, nickel coin treated with diazonium, nickel coin coated with fingerprint and post-treated with diazonium were analyzed using XPS (Fig. 1a-d). A fingerprint sample of the right thumb was collected. We differentiate the fingerprint side and the non-fingerprint side of the nickel sample by looking at the survey scan and observing the shape of the background between 600-900 eV on the binding energy scale. In this region, the inelastic background is ascending from the lower to the higher binding energy side, therefore testifying for a more screened substrate due to the co-existence of both the fingerprint and the diazonium reaction products (Fig. 1a). This is the same situation if one inspects the narrow Ni2p region

(Fig. 1b); it shows a higher inelastic background at high binding energy side (low kinetic energy side).

Ni2p (~852.9 and 855.3 eV) from the nickel coin (Fig. 1b), indicates the co-existence of both nickel in the metallic and the oxidized states, respectively. Indeed, the main Ni2p_{3/2} peak from the oxide is broad and has a satellite characteristic of Ni(II). Au4f (Fig. 1c) and N1s (Fig. 1d) correspond to diazonium and/or the fingerprints. N1s region (from Ni coin with fingerprint and diazonium) has two main peaks at about 399.8 and 405.7 eV assigned to -N=N- from the aryl groups within the aryl layer and the fingerprints, and the NO₂ group from the diazonium, respectively (Fig. 1d). In samples containing fingerprints, Ni2p has the lowest atomic percent because, compared to cleaned, bare coins, the nickel is attenuated by both the fingerprint and the aryl/gold deposits. Therefore, we no longer observe the components due to N1s from the diazonium group N₂⁺;¹² this accounts for the spontaneous reduction of the diazonium cation on nickel, a result that is in line with the spontaneous arylation of nickel reported for NBD BF₄.⁷ These XPS results, demonstrating attenuation of N1s from diazonium compound, parallel the direct observation of bubbles (Fig. 1e) when a drop of diazonium solution is gently deposited on nickel with or without fingerprint. Au4f_{7/2} (Fig. 1c), centered at ~84.1 eV, accounts for metallic state gold (NIST XPS database, <https://srdata.nist.gov/xps/>) and thus a reductive process affecting AuCl₄⁻ anions.

Fig. 1. (a) XPS survey scan of fingerprint and NO₂-aryldiazonium-AuCl₄ treated nickel sheet, (b) high-resolution Ni2p, (c) and Au4d spectra, (d) peak-fitted N1s from the coin with diazonium visualized fingerprint, and (e) digital photograph of latent fingerprint demonstration using NO₂-aryldiazonium-AuCl₄ solution on nickel coin. N1s peak fitting parameters for N1s(azo) and N1s(NO₂): peak position = 399.8 / 405.7 eV; FWHM = 2.8 / 1.85 eV.

The surface compositions of materials are reported in Table 1. The table considers the unique elemental markers of the diazonium compound and the nickel substrate. Diazonium reacts to yield metallic gold and aryl groups represented by the unique NO₂ type of nitrogen. Ni2p accounts for both the metallic and oxidized states of nickel. We report NO₂/Ni and Au/Ni atomic ratios on the one hand, and the absolute Ni at.%, on the other hand. It is clear that the total nickel content drastically decreases at the surface after placing the fingerprint and further reacting the substrate with the diazonium salt. The fingerprint area shows lower NO₂ and gold relative to the total nickel. This point will best be discussed in the light of the SEM-EDS characterization.

Table 1. Apparent elemental composition of nickel coin on different treatments (in at.%).

Material	NO ₂ /Ni	Au/Ni	Ni
Ni coin (clean)	0	0	20.6
Ni coin (NO ₂ -Aryldiazonium-AuCl ₄)	9.56	4.02	2.14
Ni coin (Fingerprint+NO ₂ -Aryldiazonium-AuCl ₄)	4.53	3.33	2.30

Further SEM images confirm the elemental composition of the surfaces (Fig. 2 and 3). The SEM images of non-fingerprint area (Fig. 2-a) show a thin gold/aryl sheet layer on top of nickel metal, with a minor case of gold nanoclusters. Fingerprint area (Fig. 3) shows a high amount of gold nanoclustering (Fig. 3b,e) on top of nickel metal, with a minor case of gold/aryl sheet. The EDS spectra displayed account for the SEM images of both types of surfaces.

Fig. 2. SEM image (A) and elemental spectra (B) of the non-fingerprint area of treated nickel coin with NO_2 -aryldiazonium- AuCl_4 . Spectra 1-4 in (B) were taken from red circles shown in (A).

Fig. 3. SEM image (A) and elemental spectra (B) of the fingerprint area of treated nickel coin with NO_2 -aryldiazonium- AuCl_4 . Spectra 1-4 in (B) were taken from red circles shown in (A).

These results were compatible with our recent work using the gold aryldiazonium salt on the copper coin surface.⁶ The fingerprint treatment on the copper coin with the diazonium salt solution showed a clear sign of Cu(II), measured by the XPS technique, which gives the black color on the coin. This combination of fingerprints and the aryldiazonium salt allow the visualization of the latent fingerprints. Also, high quality images were observed on copper and lead surfaces using the same treatment process.¹¹ The latent fingerprint produced aided to visualize the details for the three levels of primary, secondary and tertiary fingermarks studies.

Combining all results discussed above, it is possible to schematically illustrate the situation of this latent fingerprint development (Fig. 4). Direct application of the diazonium salt solution drop on the bare nickel yields a thin coating, whereas the application of the same solution drops on the fingerprints induces aryl coating topped with gold clustering.

Fig. 4. Schematics of sample preparation, initial and final composition after 1 h standby. Initial sample preparation with fingerprints (a, left). After 1 h wait and quenching, the Au nanoparticles clustered together (a, right). Initial sample preparation without fingerprints (b, left). After 1 h wait and quenching, a sheet of Au nanoparticles and aryl was formed (b, right).

4. Conclusions

NO_2 -aryldiazonium- AuCl_4 salt solution was prepared and applied on nickel and glass surfaces. The samples were first treated with the salt solution for a measured time without any application of fingerprints and subsequently analyzed with XPS. Treated nickel samples produced N_2 bubbles on the non-fingerprint side and light lines on the fingerprint side. Treated glass did not react due to its non-reducible nature. For comparison, in Cu sample analysis, there is an indication of copper leaching through the fingerprint and gold/aryl coating, whereas in nickel sample analysis, Au tends to create nanocluster on fingerprints deposited area. Particularly on nickel surface, Au and salt solution creates a film which covers the Ni surface in the absence of fingerprints. This observation indicates the potential application of Au(III) salt solution for better detection of latent fingerprints.

This experiment highlights the unique combination of high-performance surface analytical tools (XPS, SEM and EDS) and diazonium chemistry to study the development of latent fingerprints without any external action (for example without any applied potential as done elsewhere). Aryldiazonium gold(III) salts offer fast application of fingerprints detection method and can be further applied to other systems of metal surfaces that have a reducing power.

Beyond this work, if aryldiazonium salts proved to be important compounds for surface modification in general, aryldiazonium gold(III) salts appear as unique compounds of paramount importance in “forensic surface chemistry.”

Conflict of interest

None

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TOC

Highlights

- Reduction of diazonium gold(III) salts occurs spontaneously
- Latent fingerprints can be detected on nickel coins
- XPS proved to be an excellent tool in forensic studies
- Reducible AuCl_4 anions are easily reducible on fingerprints
- One step development is presented