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Developed Latent Fingerprints via Aryldiazonium Tetrachloroaurate Salts on Copper Surfaces: An XPS Study

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Abstract

Surface studies of developed fingerprints have aided in the elimination of criminal cases before moving to the court. The combination of X-ray photoelectron spectroscopy (XPS) with the aryldiazonium gold(III), $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$, surface modifier has shown to be a novel approach in latent fingerprint detection and development for the quantification of film elements. The robust gold-aryl film was developed on the reducing chemicals excreted in the sebaceous fingerprints without the need for external stimuli, and at lesser extent after contacting the free metal surface. The concurrent reduction of the diazonium functional group and gold(III) from $[\text{AuCl}_4]^-$ developed a robust gold-aryl film which showed increasing gold(0) quantity in the time range 30 to 120 min over copper coins and model flat sheets. SEM and XRD support the presence of reduced gold on the top of the latent fingerprints and the presence of CuO resulting from the reaction of the diazonium salt with copper metal. This research combines the quantification of deposits using XPS, the surface sensitive technique for chemical analysis, in addition to the surface imaging.

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

1. Introduction

Alongside the early detection of the developed fingerprints on various types of surfaces, many efforts were put to quantitatively determine the chemical components existing in latent fingerprints.^{1,2} One of such efforts includes the use of X-ray photoelectric spectroscopy (XPS).^{3,4} Since the 1980s, XPS has gained momentum in forensic science in the analysis of explosives.⁴⁻⁸ According to Watts,⁹ the use of XPS in fingerprint analysis was first recorded in 1970 by David Clark and David Briggs as an experiment performed to their local newspaper (Newcastle, England). The local newspaper at the time misunderstood that XPS may accurately track the ownership of the fingerprints in real time to catch escaping burglars. Despite this amusing misconception, Watts suggested that XPS may help identify potential suspect when characteristic materials persist on the suspect's fingerprints that may be readily transferred as well to the surface alongside with the fingerprints. An example would be the XPS peaks showing Si2p and Si2s from a sample of female fingerprints. Silicon is often used in cosmetics and skin products; thus, Si peaks may act as a potential route to identify the use of certain products by the suspect. Such profiling information from XPS can considerably reduce the suspect pool.

There are a few techniques which aided the development of forensic science and moving this emerging field from being dependent on merely qualitative to quantitative. The recent progress utilized FTIR,^{10,11} mass spectrometry,^{12,13} fluorescence,^{14,15} X-ray fluorescence^{12,16} in addition to imaging approaches.¹⁷ XPS has been introduced as surface technique for elemental analysis.¹⁸⁻²⁰

A recent report proposed an interesting method of demonstrating latent fingerprints on reactive metal surfaces using diazonium salts stabilized by tetrachloroaurate ion, NO₂-

aryldiazonium-AuCl₄.²¹ Authors used imaging techniques such as SEM, XRF and optical microscopy to visualize the change on common metals of crime scenes. It was concluded from the study that copper surface is the most successful among the three reducing metals copper, aluminum and zinc. The gold film aided to visualize the three levels of primary, secondary and tertiary fingermarks at high level of details. Reduced gold on fingerprints can be beneficial in archiving and future analysis. It is to note that poor development of the latent fingerprint was noted with aryldiazonium tetrafluoroborate (4-O₂NC₆H₄N₂⁺BF₄⁻), on the one hand, and poor contrast images with scattered minor deposits slowly occurred after an elapsed time of 24h after deposition of the reactive aryldiazonium solution. Despite the successful use of aryldiazonium tetrachloroaurate for the visualization of the fingerprints, the recently published paper focused mainly on imaging techniques. As the demonstration of fingerprints using diazonium salts on easily reactive materials (e.g. copper) is a surface chemical reaction, we anticipated that the combination of diazonium chemistry and XPS would be an original and unique method to investigate. Indeed, it is well known that aryldiazonium salts reduce spontaneously on copper²² and for the demonstration of proof of concept, this would be an ideal combination to track by XPS surface modification of copper coins (Euro cents) resulting from diazonium chemistry. The rationale for this motivation is that elsewhere, the surface analyses might take requires heat²³ or application of an electrical potential to enhance visualization of the said fingerprints.²⁴ Herein, and as some of us have previously reported, the latent fingerprints are demonstrated spontaneously without any physico-chemical assistance, which facilitates the whole study and subsequent XPS analysis.

In this study, we have cleaned copper coins and model flat copper sheets and affixed fingerprints of a donor. The fingerprints were developed with aryldiazonium tetrachloroaurate

aqueous solution for 1h. After washing, the copper coins and flat surfaces were analyzed by XPS. We will tackle two main aspects: (i) surface chemistry of aryldiazonium tetrafluoroborate salts, and (ii) XPS analysis of the positive and negative parts of the developed parts of the fingerprint on copper coin and model flat surface (Figure S1). We will then concentrate on our results of the selective binding phenomena between diazonium and fingerprints on top of copper metal. As our work is focused on fingerprints within the framework of forensic science, we have chosen to conduct surface chemical reactions on copper coins (Euro cents) in order to replicate a “real world” scenario. Some specific experiments have also been conducted on model, flat copper plate.

2. Experimental Section

Reagents. The reagents were used without any further purification: hydrochloric acid (Carlo Erba, 37%), nitric acid (Carlo Erba, 65%), 4-nitroaniline (Sigma-Aldrich, $\geq 99\%$) and sodium nitrite (Sigma-Aldrich, $\geq 97\%$).

Synthesis and characterization of $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$. 4-Nitroaniline (0.691 g, 5.0 mmol) was dissolved in 28.0 mL of 6.0 M HCl and the solution was cooled to 4.0 °C. Afterwards, NaNO_2 (0.345 g, 5.0 mmol) was dissolved in 5.0 mL of deionized water and added to the previous solution after it was cooled to 4.0 °C. The reaction mixture was stirred for 30 min at 4.0 °C. Next, $\text{H}[\text{AuCl}_4]$ was dissolved in 10.0 mL of water at 4.0 °C and added dropwise to the previous reaction mixture and was stirred for an additional 1 h at room temperature. The precipitate was recovered by suction filtration and dried to yield a bright yellow precipitate (1.076 g, 44.1%). Finally, the product was dissolved in water to form a 0.001M solution which was used in all fingerprint development studies. The salt was characterized by ^1H NMR

$((\text{CD}_3)_2\text{CO}$, 298K): δ (ppm) 9.28 (d, $^3J = 8.8$ Hz), 8.90 (d, $^3J = 8.8$ Hz); ^{13}C NMR $((\text{CD}_3)_2\text{CO}$, 298K): δ (ppm) 155.05, 135.65, 127.46, 122.12; and main ATR-FTIR bands at ν_{max} (cm^{-1}) 2280 ($\text{N}\equiv\text{N}$ stretch), 1537 (NO_2 asymmetrical stretch), 1349 (symmetrical stretch of NO_2), 1315 (C-H in plane deformation).

Deposition of $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ on copper coins. Copper coins (€0.20) surfaces were prepared by cleaning with distilled white vinegar (~6-8%) and table salt to remove the oxides, sonification to remove any dirt and then washed with absolute ethanol. The following samples were prepared for XPS analysis: Cu coin (clean); 0.001 M $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ solution was dropped using a dropper on Cu coin+fingerprint (1 h). The surface was then washed gently with deionized water until the excess salt was completely washed away and dried. The sample formed a film just enough to cover the suspected area.

Deposition of $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ on copper sheets. Three copper sheets (1 cm^2), and one copper slit ($5 \times 1\text{ cm}^2$) were prepared by cleaning with distilled white vinegar and table salt to remove the oxides, sonification to remove any dirt and then washed with absolute ethanol. The following samples were prepared for XPS analysis: Cu sheet (clean); Cu sheet+fingerprint; Cu slit was immersed partly ($1 \times 1\text{ cm}^2$) for 30 min. The slit was then immersed further, and the process was repeated for a total of 2 h, resulting in a surface with multiple layers of diazonium salt (clean, immersion for 30, 60, 90, and 120 min). The 0.001M $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ solution was dropped using a dropper on each of the prepared surfaces: Cu sheet+fingerprint (2 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.

Characterization. Infrared spectra were recorded using a Nicolet Magna-IR 550 spectrometer in the attenuated total reflection (ATR-FTIR) mode in the 4000-450 cm^{-1} range.

XPS spectra were recorded using a K Alpha apparatus (Thermo) fitted with a monochromatic Al $\text{K}\alpha$ X-ray source (spot size: 100 μm). The pass energy was set to 200 and 80 eV for the survey spectra and the narrow regions, respectively. The composition was determined using the manufacturer sensitivity factors. The copper coins and the model flat samples were mounted on the sample holder and clipped (Figure S2). The size of the microfocused beam was set to 100 μm , sufficiently low to analyze different parts of the coins, or the flat samples. Where reaction with diazonium occurred, black spots could be analyzed (Figure S3a). Also, the fingerprints showing alternating dark and light lines could individually be analyzed (Figure S3b).

NMR spectra were recorded using a Bruker Avance II spectrometer operating at a resonance frequency of 400 and 100 MHz, respectively. For ^1H NMR analysis, $(\text{CD}_3)_2\text{CO}$ was used as a solvent and internal standard. 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.

3. Results and Discussion

3.1. Rationale and procedure for visualization of fingerprints using aryldiazonium tetrachloroaurate salt

In the recent years, aryldiazonium salts of tosylates,²⁵ triflates²⁶ and tetrachloroaurate^{27,28} series emerged as very stable and safe, as they could be stored at room temperature; they are even stable up to 80-100 °C, triflates could be stable after decades as has just been claimed.²⁶ This is a tremendous progress in the chemistry of diazonium salts. Whilst most of diazonium salts are soluble in aqueous media and react with surfaces to form surface-aryl interfacial bonds, what makes the tetrachloroaurate series unique is that the reduction of the salt affects both the diazonium cation and AuCl_4^- . If the reduction is conducted in solution, one obtains gold nanoparticles grafted with aryl functional groups. However, if the reduction is conducted in the presence of a substrate, one is faced with a more complex situation in the sense that both gold and aryl groups react and deposit on the surface but not necessarily a film of gold-aryl nanoparticles is formed. This is what we will investigate in depth in the following sections. One way to contribute to the study and visualization of fingerprints is by combining diazonium salts and XPS. Diazonium salts react spontaneously on surfaces with reducing power; this is why we have selected copper coins (2 euro cents, unless otherwise stated). The choice of the nitrobenzenediazonium cation lies in the ability to provide a unique elemental marker for the aryl groups after reaction of the parent diazonium salt with the surface. As a matter of fact, NO_2 group is featured by N1s at ~406 eV. This unique marker permitted to Pinson and co-workers in 1992 to demonstrate that passivation of electrodes was due to nitrophenyl groups.²⁹ In this sense, XPS is a very surface sensitive technique and could be employed in this work with a microfocused beam, so that we could analyze both the positive and negative fingerprints after reaction of a aryldiazonium tetrachloroaurate aqueous solution with cleaned copper coins and model flat samples.

3.2. Synthesis and characterization of $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ salt.

Aryldiazonium tetrachloroaurate salt was synthesized for the purpose of this study because it gives a specific NO₂ N1s peak in addition to Au4f from metallic gold obtained by reduction at the copper surface. These features are well distinguished in XPS from Cu2p peak due to the underlying copper coin or plate. ¹H NMR characterization in deuterated acetone showed two distinct doublet of doublet peaks at $\delta = 8.90$ ppm and $\delta = 9.28$ ppm, each with clear H integration of 2H. The first peak at $\delta = 8.90$ ppm appears as a strong doublet which corresponds to the hydrogen atoms closer to N $\equiv$ N⁺. The second strong doublet at $\delta = 9.28$ ppm corresponds to the hydrogen atoms closer to NO₂. It should also be noted that at the time of the analysis, two short peaks started to form at $\delta = 8.00$ ppm and $\delta = 6.75$ ppm, indicative of the reducible nature of diazonium salts. The analysis was redone after two days and the two peaks were stronger and sharper. This observation serves as a further evidence of the low shelf-life nature of the diazonium salt in solution at room temperature. FTIR spectra showed three significant peaks. First peak at 2280 cm⁻¹ corresponds to the N $\equiv$ N⁺ (strong) stretching frequency. The second peak at 1600 cm⁻¹ corresponds to the aromatic C=C (weak) stretching frequency. The third peak came at 1400 cm⁻¹ corresponds to the C-N (medium-weak) stretching frequency.

Figure 1. (a) XPS survey scan of 4-O₂NC₆H₄N₂⁺AuCl₄⁻, (b) peak-fitted high-resolution Au4f spectra, (c) N1s.

XPS spectra of 4-O₂NC₆H₄N₂⁺AuCl₄⁻ (Figure 1) displays high resolution Au4f and N1s (Figure 1b and 1c, respectively); Au4f has two doublets assigned to 4f_{7/2} and 4f_{5/2} in the 4/3 ratios, assigned to Au(0) (85 and 89 eV) and Au(III) (87 and 91 eV), respectively. The N1s peak is fitted with four components centered at 400.7, 404.1, 406.0 and 408.2 eV assigned to reduced nitrogen species, neutral N in N₂⁺ group, NO₂, and possibly NO₃⁻ contamination that might occur during the synthesis of H[AuCl₄] using aqua regia. Although the diazonium product was thoroughly washed, we have invariably observed nitrates, nevertheless at low extent. The peak at 400.7 eV arises from the in-situ X-ray induced reduction of the salt during XPS analysis and

could be assigned to -N=N- species. The peak at 406 eV combines NO₂ from the nitrobenzene and the positively charged N in the N₂⁺ group.

3.3. XPS analysis of surfaces developed by fingerprints

3.3.1. Surface study on copper coins. A sample consisting of a copper coin (2 € cents) with diazonium and fingerprints was analyzed using XPS as a means of a preliminary assessment (Figure 2). Fingerprint samples from 12 different areas of the right thumb were collected after hand washing with soap, thorough tap water rinsing and hand drying. The composition of the deposited materials on the copper surface is summarized in Table S1. Cu2p_{3/2} (avg. 932.5 ± 0.17 eV) corresponds to the copper coin, whereas Au4f_{7/2} (avg. 84.2 ± 0.02 eV) corresponds to gold deposits by spontaneous, in situ reduction of the aryl diazonium tetrachloroaurate salt. As shown in Figure 2b, the area under the curve of each position fluctuates as one moves from fingerprint to non-fingerprint region, these data initially showcase the selectivity nature of diazonium towards the fingerprint region. N1s region has two main peaks: one at (avg. 399.9 ± 0.13 eV), assigned to (-N=N-) from the aryl functional groups within the aryl layer and the fingerprints, and (avg. 406.0 ± 0.07 eV), assigned to the NO₂ group from the diazonium. The N1s region thus shows that the diazonium cation has been reduced and this region is left only with two main components from azo and NO₂ groups, and disappearance of diazonium N1s signals. Cu2p XPS spectra shows (Figure 2a) the relatively low atomic percentage because, compared to cleaned coins, the copper is attenuated by both the fingerprint and the aryl/gold deposits.

Figure 2. (a) High-resolution Cu2p, (b) Au4f spectra of fingerprint and 4-O₂NC₆H₄N₂⁺AuCl₄⁻ treated copper coin on 12 different areas.

3.3.2. Surface study on model copper sheets. Recently, Lafi. *et al.*³⁰ discussed a phenomenon that occurs when applying aryldiazonium salt solution on a metal surface for a prolonged period. The authors found that the salt solution may further react with the metal after initially binds with the fingerprint. As a result, the whole area of metal covered with the solution turned dark instead of the predicted appearance of observable dark print of the fingerprints. Thus, we were interested in investigating the driving force behind this phenomenon. Towards this end, four samples of copper sheets were treated with the aryldiazonium gold salt, each with different treatment time of 30, 60, 90 and 120 min. The samples were subsequently characterized using XPS (Figure 3 and Table 1). As reported in Table 1, the relative atomic percentage of Au (computed using Au 4f doublet with Au 4f_{7/2} at ~84 eV due to Au(0)) increases with treatment time (Figure 3b). This is believed to be normal due to the natural tendency of Au deposition as the solution reacts with the metal for a longer period. What seems to be unusual, the relative atomic percentage of copper (computed using Cu 2p_{3/2} at 932.5 eV) also increases as the treatment time increases (Figure 3c).

This is surprising because it was expected that copper should have been covered by more deposits as time elapses, leading to less relative atomic percentage. Instead, the opposite case seems to persist, which indicates that there may be diffusion of copper species towards the surface.

Figure 3. (a) XPS survey scan of 4-O₂NC₆H₄N₂⁺AuCl₄⁻ on copper sheet at multiple time increments, (black) clean Cu, (red) after 30 min, (blue) after 60 min, (green) after 90 min, and (violet) after 120 min, (b) high-resolution Au4f spectra, (c) Cu2p peak.

Table 1. Elemental composition of copper sheet at different time increments.

Material		C 1s	NO ₂	-N=N-	Cu 2p _{3/2}	Au 4f
Cu slit (Clean)	Peak BE	285.1	408.0	400.0	932.6	90.7
	Atomic %	74.1	0.4	4.9	20.6	0.0
4-O ₂ NC ₆ H ₄ N ₂ ⁺ AuCl ₄ ⁻ on Cu slit (30 min)	Peak BE	285.0	406.1	400.2	932.5	84.2
	Atomic %	84.6	6.9	3.3	1.4	3.9
4-O ₂ NC ₆ H ₄ N ₂ ⁺ AuCl ₄ ⁻ on Cu slit (60 min)	Peak BE	285.0	406.1	400.1	932.4	84.1
	Atomic %	83.6	7.2	3.5	1.4	4.3
4-O ₂ NC ₆ H ₄ N ₂ ⁺ AuCl ₄ ⁻ on Cu slit (90 min)	Peak BE	284.9	406.0	400.2	932.2	84.2
	Atomic %	82.2	6.7	3.1	1.6	6.3
4-O ₂ NC ₆ H ₄ N ₂ ⁺ AuCl ₄ ⁻ on Cu slit (120 min)	Peak BE	284.9	406.0	400.1	932.3	84.1
	Atomic %	80.6	6.1	3.8	2.0	7.6

To further investigate the products of the interfacial reaction between the diazonium tetrachloroaurate and copper, we have closely inspected the narrow Cu2p copper region and have taken advantage of the method devised by Biesinger³¹ to deduce Cu(II) from the Cu2p doublet. According to Biesinger, the Cu(0+I)/Cu(II) ratios for samples containing a mixture of Cu(0+I) and Cu(II) rely on estimation of the main peak/shake-up peak areas (A_{1s}/B_s) for a 100% pure Cu(II) sample (Figure 4a). With a reliable value of A_{1s}/B_s obtained for CuO (Table 2), the relative concentrations of Cu(0) and Cu(II) species present on the surface that contain both species (Figure 4b) can be obtained using Equations 1 and 2

$$\% \text{ Cu(0 + I)} = \frac{A - \left(\frac{A_{1s}}{B_s}\right) B}{A + B} \times 100\% \quad 1)$$

$$\% \text{ Cu(II)} = \frac{B \left(1 + \left(\frac{A_{1s}}{B_s}\right)\right)}{A + B} \times 100\% \quad 2)$$

where A is the total area of the main peak and B is the area of the shake-up peak of the sample.

Figure 4. (a) XPS survey scan of a pure CuO sample, (b) peak-fitted high-resolution Cu2p spectrum.

Table 2. Tabular representation of XPS data of a pure CuO sample (top) and ratio of the main peak/shake-up peak areas (A1s/Bs) for a 100% pure Cu(II) sample (bottom).

Name	Peak BE	Atomic %
C1s	284.6	14.7
C1s B	285.8	2.13
C1s C	287.53	1.33
C1s D	288.8	1.51
Cu2p _{3/2}	933.0	14.1
Cu2p _{3/2} B	934.7	7.82
Cu2p _{3/2} (Shake-up)	940.6	4.8
Cu2p _{3/2} (Shake-up) B	942.0	1.98
Cu2p _{3/2} (Shake-up) C	943.5	3.67
Cu A	568.5	0.0
O1s (CuO)	529.4	29.7
O1s B	531.3	14.8
O1s C	532.9	3.42
A1	B1s	A1/B1s
Cu2p _{3/2}	Cu2p _{3/2} (SH)	Cu2p _{3/2} / Cu2p _{3/2} (SH)
191643.74	90567.96	2.116

Next, a sample of a copper sheet treated with fingerprint and diazonium salt was analyzed (Figure 5 and Table S2). The reaction of the diazonium aqueous solution with copper yields positive dark lines after only 15-20 minutes, and bubbles are visible between the fingerprint lines (Figure 5e). As detailed in the Experimental section, 100 μm spot size was used in order to analyze the dark and the light lines without any interference. An XPS spectra was collected from four different areas of the now-visible fingerprint sample (P2D and P4D: fingerprint area, P1L and P3L: non-fingerprint area), it was easy to differentiate the fingerprint (D for dark) side and the non-fingerprint (L for light) side of the copper sample by looking at the survey scan and observing the shape of the background in the range 700-900 eV (Figure 5). The composition of materials on the sample surfaces are summarized in Table S2.

Remarkably $\text{Au}4\text{d}_{5/2}$ (Figure 5d), centered at 335.1 eV, accounts for metallic state of gold and thus a reductive process affecting $[\text{AuCl}_4]^-$ anions.³² Similarly, Figure 5c shows only two peaks for nitrogen, one centered at 400 eV and one at 406 eV assigned to $-\text{N}=\text{N}-$ within the aryl layer and NO_2 , respectively. Therefore, we no longer observe the components due to N1s from the diazonium group N_2^+ . This accounts for the spontaneous reduction of the diazonium cation on copper. These XPS results parallel the direct observation of bubbles (Figure 5e) when a drop of diazonium solution is gently deposited on copper with or without fingerprint.

Figure 5. (a) XPS survey scan of fingerprint and 4-O₂NC₆H₄N₂⁺AuCl₄⁻-treated copper sheet on four different areas, (b) high-resolution Cu2p, (c) N1s, (d) Au4d spectra, (e) Latent fingerprint demonstration using diazonium solution on a copper sheet. Bubbles correspond to the release of N₂ due to the spontaneous reduction of diazonium cation.

3.4. Scanning electron microscopy of latent fingerprint after reaction with aryldiazonium tetrachloroaurate

Further SEM images display the morphology of the surfaces (Figures 6 and 7). The SEM images of non-fingerprint area (Figure 6a) show minor gold nanoclustering (Figure 6b, c, f) on top of copper metal (Figure 6d, e). Fingerprint area investigated using EDS (Figure 7a) shows an interesting composition of what seems to be CuO (Figure 7b, O = 34.0% Cu = 32.8%) on top of copper (Figure 7c), in addition to a minor gold nanoclustering (Figure 7d).

Figure 6. SEM image (a) and EDS elemental spectra (b-f) of the non-fingerprint area of treated copper sheet with $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$.

Figure 7. SEM image (a) and EDS elemental spectra (b, c, d) of the fingerprint area of treated copper sheet with $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$.

To sum up, Figure 8 proposes a mechanistic view of the reaction of $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ aqueous solution with a copper sample without and with fingerprints after 1h standby. After 1 h wait and quenching, the fingerprint and $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$ layer merged into one with clear sign of Cu(II) of copper diffusing onto the upper layer via XPS measurements (Figure 8, right);

this what explains the occurrence of dark, black marks (the color of CuO). Initial sample preparation without fingerprints (Figure 8b, left) gives a slight change in the color of the copper coin, after 1 h wait and quenching, however without detection of Cu(II) diffusion and localized dark spots (see also Figure S2, top left coin). Obviously, it is the combination of the fingerprints and the aryldiazonium salt that permits the visualization of the latent fingerprints. Chloride ions in eccrine sweat are known to corrode copper and even noble metals after long contact (10 days) with fingerprints.³³ However, for fast visualization, the fingerprints alone do not suffice since after 1h; the fingerprint on 1 euro cent clean copper coin does not lead to the developed black lines as shown in Figure S4.

Figure 8. Reaction of clean and fingerprint-coated copper samples with nitrobenzenediazonium tetrachloroaurate aqueous solution.

Summary and Conclusions

4-nitrobenzenediazonium tetrachloroaurate, $4\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{AuCl}_4^-$, was reacted on copper coins and sheets. The samples were first treated with the salt solution for 30, 60, 90, and 120 min

without fingerprints application and subsequently analyzed with XPS. Treated copper samples produced N₂ bubbles on non-fingerprint side and dark lines on fingerprint side. Following this result, a second XPS analysis of another batch of sample surfaces of Cu treated with both fingerprints and salt solution were performed. There are strong evidences of the reduction of Au(III) to Au(0) and diazonium cation to aryl functional groups on copper samples. In copper sample analysis, there is an indication of copper leaching through the fingerprint and gold/aryl coating. Copper is leached as CuO, hence the black color of the demonstrated fingerprints. These observations indicate the potential application of Au(III) diazonium salt solution for a fast development of latent fingerprints.

This work highlights the unique combination of XPS and diazonium chemistry to study the development of latent fingerprints without any external stimuli, for example without any applied potential or heat as reported previously in the literature. Diazonium gold(III) salts offer fast application of fingerprints detection and development and can be further applied on other metal surfaces that have reducing property.

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Supporting Information

The Figures show mounting copper coins on sample holder, and selected areas analyzed by XPS. Tables reporting XPS-determined compositions of copper coins after reaction diazonium salts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC

XPS analysis of fingerprint visualized with 4-nitrobenzenediazonium tetrachloroaurate salt