

Gold Modification by Reduction of a Diazonium Salt Prepared from Aliphatic Diamine**Ahmed Ismail Kareim****Gold Modification by Reduction of a Diazonium Salt Prepared from Aliphatic Diamine****Ahmed Ismail Kareim**

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We report on the electrochemical reduction on gold electrode of diazonium salt prepared from lysine. For the first time, the covalent functionalization on gold of an alkyldiazonium salt is demonstrated and required diazotization of one amine group from lysine. The grafted organic films have been achieved and monitored using electrochemical quartz crystal microbalance (EQCM) coupled to cyclic voltammetry (CV). Infrared absorption spectra (FTIR) and high resolution X-ray photoelectron spectroscopy measurements show that the organic film is successfully attached to the surface of the gold substrate. The major advantage and interesting of this procedure is that the diazonium cation is generated closely to the electrode surface. Moreover, the attached layers were found to be stable for two months after storage at room temperature as the recharacterization of modified gold surfaces provided the existence of organic film. This process could be useful for modifying various surfaces by different types of aliphatic amine.

Keywords: alkyldiazonium, lysine, gold surface modification, HR XPS, ATR-IR, electrochemical reduction.

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تغيير خصائص سطح الذهب من خلال اختزال املاح الديازونيوم الالفاتية ثنائية الامين

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الخلاصة

تم اختزال وترسيب ملح الديازونيوم المحضر من الحامض الاميني الليسين على سطح قطب الذهب بالطرق الكهربية. تمت عملية الترسيب والترابط التساهمي مع سطح الذهب من خلال مفاعلة احدى مجاميع الامين لحامض الليسين. انجزت عملية الترسيب باستخدام تقنية الميزان الميكروي لبلورة الكوارتز المرفقة مع تقنية الفولتمتري. من جهة اخرى تم تشخيص الطبقة العضوية المترسبة على سطح الذهب من خلال استخدام اطياف الاشعة تحت الحمراء ومطيافية الاشعة السينية الفوتوالكترونية. واحد من ابرز الخصائص الفريدة لهذه الطريقة هو توليد ايونات الدايزونيوم الموجبة على مقربة من سطح القطب تم اختزالها. تم التأكد من الاستقرار الميكانيكية للطبقة العضوية على سطح الذهب من خلال خزن السطوح المعدلة لمدة شهرين في درجة حرارة الغرفة ثم اعيد فحص السطوح حيث اكدت النتائج بقاء وجود الطبقة العضوية.

الكلمات المفتاحية: الكيل الديازونيوم، ليسين، تحوير سطح الذهب، مطيافية الاشعة السينية الفوتوالكترونية، مطيافية الاشعة تحت الحمراء، الاختزال الكهروكيميائي.

Introduction

Since the late 80s, great efforts have been devoted to the modification and functionalization of surfaces. Self-assembled monolayer [1, 2], cathodic [3, 4] or anodic [5, 6] polymerization are amongst the most interesting techniques for modifying conducting and semiconducting surfaces. In this context, a promising candidate was introduced for the covalent attachment of organic molecules to surface via the electrochemical reduction of aryldiazonium salts [7]. A wide variety of substituted aromatic amines by reactive group have been used for the preparation and grafting of diazonium salt by electrochemistry [8]. The electrochemical reduction of aryl diazonium cation, which is prepared from corresponding arylamine in aqueous

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or aprotic solutions, causes cleavage of dinitrogen and generates phenyl radicals close to the interface. In turn, this later reacts with the atoms of substrate surface to form a covalent bond via carbon-metal [9, 10]. Contrary to drastic methods involving vigorous oxidation processes, ultrasonication [11], chemical reducing agents [12] or thermolysis [13], the surface modification by reduction of diazonium salt has some advantages. For instance, it has the simplest procedure, direct introduction of functional groups, and produces a persistent and resistant film. So far, the various organic layers grafted by electrochemical reduction of diazonium salts were prepared from arylamine compounds. Recently, alkyl chains have been successfully grafted on copper electrodes by the *in situ* reaction of alkyl amines dissolved in aqueous perchloric acid with nitrite ions electrogenerated from nitrate ions [14]. The present work focuses on grafting an organic thin film through electrochemical reduction of diazonium salt prepared by using aliphatic diamine (lysine) *in situ* on gold surface. This work confounds the previous perceptions that considered the preparation and grafting of diazonium salt from an aliphatic compound is impossible due to the lack of its stability compared with those prepared from aromatic compounds. For this purpose, one amine group of lysine molecules is diazotized by sodium nitrite and the other one is kept for further reactions as amine group can undergo for a variety of chemical reactions.

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Experimental section

Reagents and substrates

All chemicals were purchased from Sigma-Aldrich (France): lysine 99%, sodium nitrite, Hydrochloric acid, acetone, absolute ethanol, sulfuric acid and gold wafer. 5MHz polished gold AT-cut quartz crystals (1.37 cm²) are from Maxtek, USA. All the reagents were of analytical grade and were used without further purification. Milli-Q water with resistivity greater than 18 M Ω was used for the preparation of aqueous electrolytes. Gold-coated silicon wafers were purchased from Nanoandmore GmbH (Germany). Rectangular samples were cut (2x1) cm² and used as working electrode.

Electrochemical method

Prior to the electrografting step, the gold-coated wafers were cleaned by sequential immersion in acetone, ethanol and sulfuric acid and then rinsed with deionized water for removing organics from the gold surface. For the preparation of the diazonium salt, 1.46 g of lysine was dissolved in 100 mL of deionized water in presence of excess of HCl and one equivalent quantity of sodium nitrite (0.69 g) was dissolved in 10 mL of deionized water. The two solutions were cooled below 5°C and then the sodium nitrite solution was added dropwise to the acidic lysine solution under stirring to prepare the diazonium salt. The mixture of two solutions is transferred immediately into a conventional three electrode electrochemical cell which is held at 5°C where the working electrode is a 5 MHz polished gold AT-cut quartz crystals, the counter-electrode is a Pt wire and the silver wire was used as a pseudo-reference electrode. EQCM coupled to cyclic voltammetry which was used to monitor the mass gain during the electrochemical reduction of diazonium chloride on gold by using a computer-controlled eDAQ potentiostat (Australia), model e-corder 401. The efficient reduction potential of diazonium salt was obtained through the cyclic voltammogram as it was equal to (- 0.55V).

For avoiding the long-term storage due to the lack of its stability and in order to graft thick organic layer on gold surface, the diazonium salt was prepared in situ of gold electrode and the constant potential technique was used for reduction of diazonium cations. Therefore, another solution of lysine was prepared by dissolved the same quantity above in 100 mL of deionized water in absence of HCl and the sodium nitrite solution was also prepared as mentioned before.

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The two solutions were cooled to 5°C and then mixed by using the same electrochemical cell and kept in an ice bath such that the temperature of the mixture remains less than 5°C. The hydrochloric acid solution (0.5M) was injected slowly and directly onto gold-coated electrode surface while the gold electrode is held at -0.6 V/Ag in order to prepare diazonium ions and reduce them immediately on gold surface. The frequency variation is converted into mass variation directly from Gordon-Kanazawa's relationship [15].

Characterizations

Attenuated total reflection infrared spectroscopy (ATR-FTIR) was carried out with a PerkinElmer Spectrum Version 10.01.00 model 2010 in the laboratory of nanomedicine (France). High resolution x-Ray photoelectron spectroscopy (HR XPS) analyses were carried out on a K-Alpha spectrometer thermo electron. The monochromatic Al K α line was used as X-ray excitation (1486.6 eV) with pass energy of (20 eV) to obtain high resolution spectra. Large X-ray spots (400 μ m) were usually used to explore the surface. The homogeneity of the surface modification was also controlled on lines by using small X-ray spots (100 μ m). Spectrometer calibration was performed using the manufacturer's procedure, which was completed by a self-consistent check on sputtered copper and gold samples, based on the ASTM E902-94 recommendation.

Results and discussion

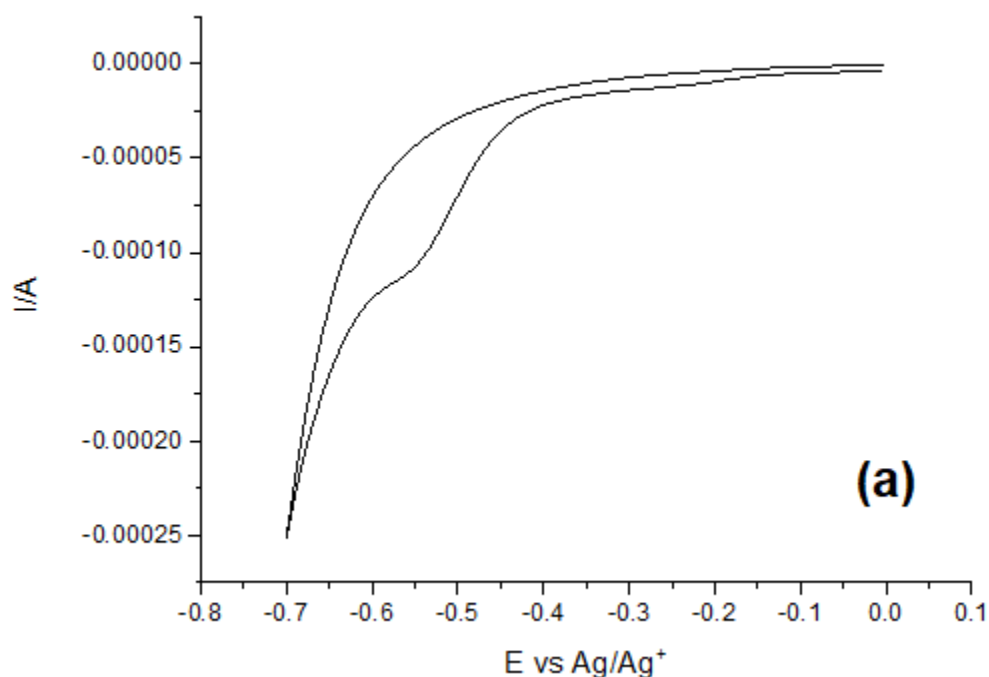
1. Electrochemical measurements

Fig. 1a shows the cyclic voltammogram for cathodic reduction of the prepared diazonium salt in aqueous acidic solution. The irreversible reduction process on gold is indicated by a large reduction peak centered at about -0.55 V yielding nitrogen cleavage [16]. Small bubbles are observed which correspond to nitrogen gas during electrolysis experiment as this confirms the cleavage of the dinitrogen. The elimination of nitrogen bubbles during the electrografting reaction is an obvious indication of generating diazonium salt of the aliphatic compound (lysine) which is considered as almost impossible to produce due to the lack in its stability. EQCM measurements coupled to cyclic voltammetry provide evidence and give further insight into the electrodeposition of lysine and the formation of an organic layer on gold surface.

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Consequently, the mass deposition can happen shortly after these cathodic peaks as it is the case Fig. 1b and in other works [17, 18]. On the other hand, it can be seen that the mass deposition at gold electrode for the first scan is greater than the other scans as the mass deposition decreasing provides a good evidence of complete coverage of gold surface. More, EQCM measurements were performed using potentiostatic method. The gold coated substrate was biased at -0.6 V and diazonium salt deposition occurs as shown with the mass vs. time graph (Fig. 1c). At constant potential, it is clear that the mass deposition on gold surface increases rapidly at the beginning of the process and tend to reach a limit after about 400 s.



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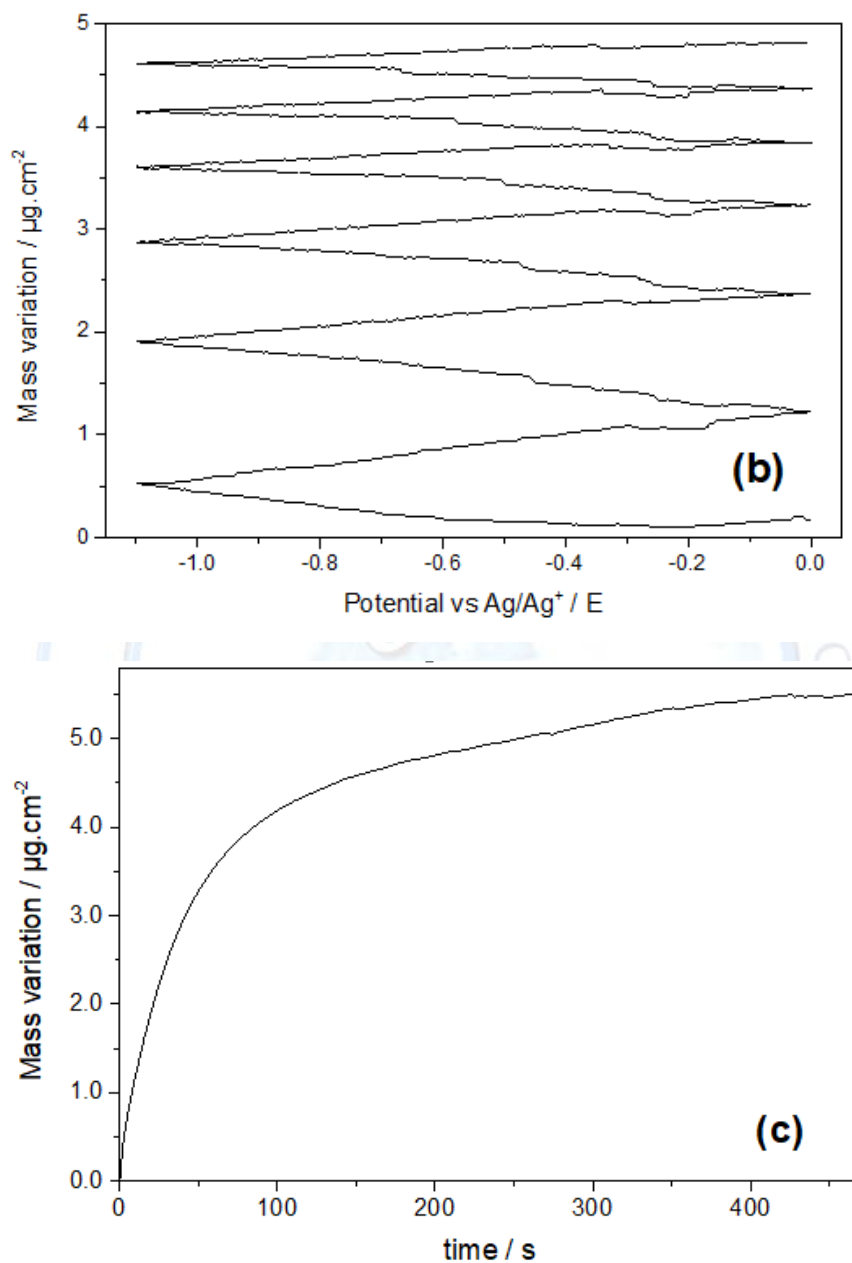


Figure 1: (a) Cyclic voltammety, (b) mass vs. potential, and (c) mass vs. time in cathodic reduction of fresh alkyl diazonium salt from lysine in aqueous acidic solution.

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2. FTIR spectroscopy

Once the electrochemical reduction experiment is achieved, the grafted gold substrate is rinsed with deionized water and then submitted to ultrasonic treatment (40°C for 20 min in water). The goal is to check the resistance of the deposited layer and to remove any unreacted molecules which could be loosely attached to the surface. The deposited organic layer is strongly attached to the gold surface. ATR-FTIR and XPS techniques were used to characterize the resulting organic film and were also used to characterize the grafted gold surface with organic film obtained from diazonium salt which stores for two months under ambient conditions.

To confirm the attachment of organic film on gold surfaces, the modified gold plate was examined by ATR-IR as shown in Fig. 2. Evidence for the presence of carboxylic and alkylamine groups on the gold electrode surface is clearly observed with characteristic bands. The asymmetric and symmetric stretching vibration modes of CH₂ between (2920 and 2860 cm⁻¹), and the band at (1450 cm⁻¹) attributed to the bending of CH₂ group are related to the presence of the alkyl group. The broad peak at 3400 cm⁻¹ and the other one at (3200 cm⁻¹) are characteristic of the primary amine group. The NH₂ scissoring vibration found at (1570 cm⁻¹) confirms the presence of amine function as terminal group. The absence of significant band in the (2300-2130 cm⁻¹) region for the stretching of the N≡N bond in the diazonium salt, confirms the loss of dinitrogen during the electrografting process [19].

The bands at (1640 and 1450 cm⁻¹) are attributed to asymmetric vibrations of NH₃⁺ which could be involved in ionic interaction with HCO₃⁻ derived from atmospheric CO₂ as previously hypothesized by Culler et al. Additionally, the absorption band centered at (1735 cm⁻¹) is a characteristic of the carbonyl group[20].

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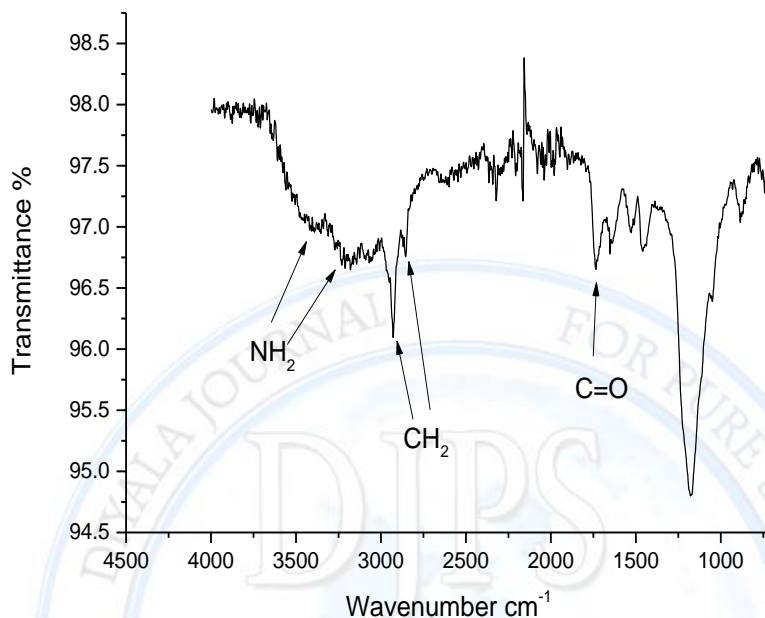


Figure 2: ATR-IR spectra of modified gold-coated quartz with organic film contains carboxyl and ethylamine groups.

3. HR X-Ray photoelectron spectroscopy

HR XPS measurements have been performed to ascertain the modification of gold surface plates with the resulting organic layer. The obtained results of XPS proved the presence of nitrogen, carbon and oxygen elements (Fig. 3) and this is definitely a good indication for gold surface grafting. Two peaks at (400 and 402 eV) (Fig. 3a) are attributed to N 1s core level and clearly indicate the presence of two types of nitrogen in the grafted organic layer. The first one is assigned to unprotonated amine group (NH_2). The second one may indicate the presence of $-\text{C}-\text{N}=\text{N}-\text{C}-$ group and this could be a good indicative for multilayer formation [22]. This second peak may be also attributed to protonated amines NH_3^+ [23]. The C 1s core level shows four peaks (Fig. 3b). The first one is centered at (284.7 eV) which corresponds to C-C. The peaks at (286 and 287.2 eV) are assigned to C-O and C- NH_2 groups, respectively. The fourth peak at (288.5 eV) is related to carbon atom of the carbonyl group. These results are in

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agreement with those obtained by ATR-FTIR which indicated the presence of carbonyl group [24]. The peak centered at (532.4 eV) (Fig. 3c), is assigned to O 1s region and may be explained by the formation of ammonium bicarbonate structure following the reactions between amine, atmospheric carbon dioxide and water [25, 26]. Moreover, the presence of Au 4f_{7/2} spectra at (84 eV) (Fig. 3d) indicates that the deposited organic layer is ultrathin and does not completely shield the gold surface. The modification of gold surface by *in situ* generated alkyl diazonium salt, might yield to a grafted film containing some impurities compared with the conventional procedure, where some insoluble species grafted on gold surfaces, generated by dissolving diazonium salts in protic or aprotic solvents [27].

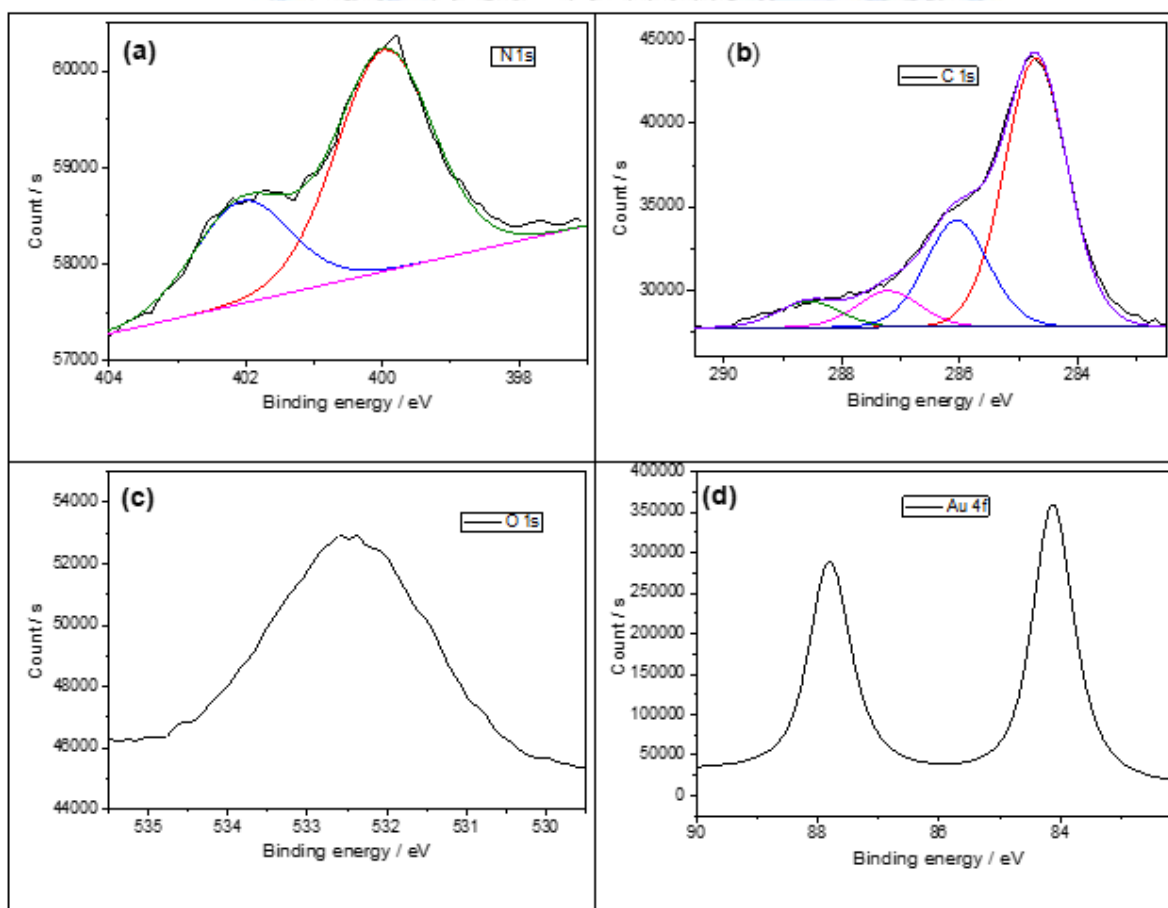


Figure 3: HR XPS core level spectrum of the regions of (a) N 1s, (b) C 1s, (c) O 1s and (d) Au 4f, from gold surface modified with alkyl diazonium salt contains carboxylic acid and alkylamine groups.

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Conclusion

The electrochemical measurements, ATR-FTIR, and XPS analysis pointed out the grafting of an organic film onto gold surface by electrochemical reduction of alkyl diazonium chloride prepared beforehand by diazotization of one lysine amino group. The mechanical stability and the strong attachment of the organic layer on gold surface have been confirmed by sonication treatment. This test provided further evidence for a film bound firmly with gold surface and given indirect proof of the existence of a covalent bond. The modified gold plates were investigated by ATR-FTIR, and XPS techniques after being ultrasonicated in water bath at 40°C. On the other hand, the grafted gold surface with organic film obtained from diazonium salts has been characterized after storage for two months under ambient conditions. Results indicate the existence and stability of the electrodeposited organic film.

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