COVALENT MODIFICATION OF GOLD THIN FILMS FOR PLASMONIC APPLICATIONS: COMPARISON OF SPONTANEOUS AND ELECTROGRAFTING

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Abstract

Surface modification by the attachment of organic groups is a subject of current interest in material science and sensor design. We developed facile procedure for covalent functionalization of optical-active gold thin films using water-soluble arenediazonium tosylates (ADTs). These strongly bonded organic layers were characterized by IR, XPS, water contact angles, AFM, SEM-EDX, UV-Vis, CVA and SERS. According to structural characteristics, spontaneous interaction of ADTs water solution with metal-coated substrates gave close to monolayer organic film. Whereas electrochemical reaction in aqueous media resulted in multilayer coating. Observed shift of plasmon resonance and ehnhanced Raman intensity after modification by ADTs enables to consider prepared materials as a platform for sensing system. Plasmon-active metal surfaces decorated with immobilized organic functional groups can be applied as selective SPR or SERS sensory elements for the detection of trace amounts of bioorganic compounds, toxins and pollutants via further functionalization by molecular recognition elements or as tunable plasmonic devices.

1. Introdction

Taking into account the distribution of plasmon intensity, coverage of surface by oganic molecules is standing out as a key point for successful plasmonic device realization. The thickness of organic layer must be carefully chosen, depending on the on different applications scenarios. In particular, the SERS and SPR applications requires surface functionalization by the thin molecular layer, to conserve the maximal interaction of plasmon with analyte, which interact with modified metal surface [1, 5]. Oppositely, for plasmonic laser or switches full covering of surface by the attached organics molecules is desired. So, in this case, the “thick” layer of organic compounds is preferred [2-4]. Thus, development of surface modification method with controllable resulting thickness of organic layer is still challenging for plasmonic metal surfaces [6]. Chemical functionalization by thiol derivatives is one of the most commonly used approaches for the decoration of plasmonic substrates with organic functional groups (OFGs) [7,8]. However, a number of authors underlined disadvantages of this strategy - moderate stability (including thermal one) of metal-thiol bonds due to chemisorption nature of binding, only formation of monolayers, reversibility, possibility of displacement by other thiols and poor availability of commercially available modification substrates [9,10].

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An attractive alternative to thiol's chemistry is the grafting of OFGs by arenediazonium salts (ADSs) because high reactivity of the aryl radicals results in the generation of aryl layers strongly covalently bounded to metal surface [11-14]. This strategy is well-proven for a wide range of materials, including metal and polymer substrates and enables to create a strong covalent linker between the surface and a variety of biomolecules, ligands, and other organic compounds [15]. The majority of works are directed to modification of metal electrodes or plates using ADSs, but the modification of thin, plasmon-active metal films are left unattended yet [16,17].

In this work (see Figure 1) we demonstrate surface modification of thin silver and gold films by spontaneous reaction and electrochemical reduction of water-soluble arenediazonium tosylates (ADTs). After grafting the surface and optical properties were characterized by the wide range of techniques. We conducted detailed comparative research of surface properties on prepared materials and hypothesized appropriate modification conditions for certain optical application.

2. Material and methods

2.1 Materials and samples preparation

Gold was deposited onto glass surface (Thermo Scientific), covered by transparent titan layer (thickness cca 10 nm) ,using vacuum sputtering method (DC Ar plasma, gas purity - 99.995 %, gas pressure 4 Pa, discharge power 7.5 W, sputtering time 120 sec). Targets for metals deposition (purity of metals 4 N) were purchased from Safina. 4-nitrobenzenediazonium tosylate, 4-carboxybenzenediazonium tosylate, 4-aminobenzenediazonium tosylate and 4-(heptadecafluorooctyl)benzenediazonium tosylates were prepared according to published procedure [18]. The 4-nitrophenyl, 4-carboxyphenyl, 4-aminophenyl and 4-(heptadecafluorooctyl)phenyl organic functional groups (OFGs) were grafted spontaneously by soaking of the freshly obtained Au films in 1 mM freshly prepared solutions of corresponding arenediazonium tosylates in water for 10 min (for 4-(heptadecafluorooctyl)benzenediazonium tosylate mixture of water/ethanol (3/1) was used). Electrografting of Au was performed in 1mM fresh water solutions of corresponding diazonium salts (for 4-(heptadecafluorooctyl)benzenediazonium tosylate mixture of water/ethanol (3/1) was used) without addition of any electrolytes under the potential -2 V for 10 min with a platinum counter electrode. After modification metal substrates were rinsed under sonication sequentially with water, ethanol and acetone for 10 min and dried in desiccator for 3 hours.

2.2 Measurement techniques

Water contact angles were measured by goniometer Surface Energy Evaluation System (Masaryk University, Czech Republic) at 10 positions with distilled water at room temperature in 72 h after surface modification.

An Omicron Nanotechnology ESCAProbeP spectrometer was used for determination of surface elements concentration from X-ray induced photoelectron spectra (XPS). The analyzed area had dimensions of 2x3 mm^2. Concentrations of elements were calculated in at. %.

Cyclyc voltamperometry.(CVA) curves of pristine and modified films were obtained using 1 mM potassium hexacyanoferrate (II) in 1 M (p.a., Lachema, Czech Republic) potassium chloride for gold films (p.a., Lachema, Czech Republic). Voltammetric measurements were performed with portable potentiostat PalmSens (Palm Instruments, Netherlands), controlled by PSTrace 4.6.1 software (4.4 firmware). Parameters of the CV potential program were: 50 mV s^{-1} scan rate and potential range from -100 mV to 600 mV for the gold films. All measurements were repeated three times with five scans for each measurement, unless stated otherwise.

UV-Vis spectra were measured using Spectrometer Lambda 25 (Perkin-Elmer) in 300-1100 nm wavelength range.

Raman scattering was measured on Nicolet Almega XR spectrometer (Laser power 15 mW) Raman spectrometers with 470 and 785 nm excitation wavelengths. Spectra were measured 10 times, each of them with 30 s accumulation time.

3. Results and discussions

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In the present work we report comprehensive study of structure and surface properties of plasmonic active Au films functionalized by ADTs (see Figure 1), which possess a key advantage over classical diazonium salts [19,20]. Firstly, the metal surfaces were modified by 4-nitrobenzenediazonim tosylate (ADT-NO_2) and 4-(heptadecafluorooctyl)benzenediazonium tosylate (ADT-C_8F_{17}) as the model modification agent (due to a large basis of data about these compound grafting and significant changes of surface properties after introduction of perfluoro-derivatives) [21]. Secondly, modification by 4-aminobenzenediazonium tosylate (ADT-NH_2) and 4-carboxy benzenediazonium tosylate (ADT-COOH) was investigated because these functional groups are able to create specific surface properties or selective sites for further modification by a wide range of ligands and biomolecules. Taking into account different potential application of the plasmonic surface modification, which can requires monomolecular or polymolecular layers of grafted compound, the surface modification was performed by two procedures, shown schematically in Figure 1.

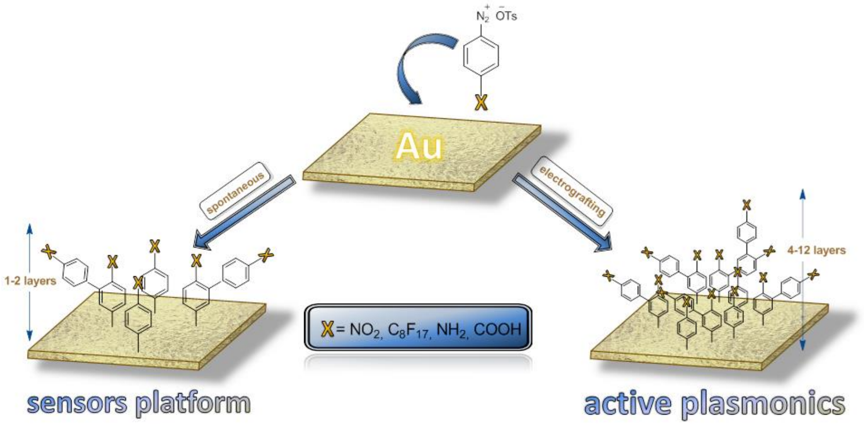

Figure 1. Schematic representation of the proposed covalent modification of plasmon-active gold surface

Modification mechanisms usually involve dediazoniation leading to spontaneously generation of reactive cations or radicals, which are able to graft spontaneously on electron-rich surfaces such as metals and, in this case, closed to monomolecular layers are formed [22,23]. Oppositely, electrically induced proces results in thicker and more disordered organic layers due to enhanced reduction of ADSs [24, 25]. Thus, application of spontaneous surface modification will leads to the formation of thin layer, suitable for sensoric applications, and the electro-induced modification will create thicker layer applicable e.g. in plasmonic-based switchers or lasers.

The changes in surface elemental concentration after OFGs grafting were studied using XPS method. On the pristine sample the presence of carbon and oxygen traces is apparent, indicating the sputtering deposition imperfection which is typical case for the deposition of metals by sputtering procedure. In XPS spectra typical peaks for grafted OFGs are observed in accordance with the results published previously [10, 26]. As could be expected, the electrochemical grafting resulted in greater concentration increase of carbon, nitrogen and fluorine concentrations comparing to spontaneous modification. Grafting of ADT-NO_2 resulted in the appearance of nitrogen-related XPS peak. Grafting of ADT-C_8F_{17} groups led to similar result i.e. apparently higher concentration of fluorine in the case of electro modification.

Thicknesses of grafted organic layers were measured by scratch method using the AFM technique. The layer thickness after modification with species of known molecular size enables one to discern the grafting of mono or polymolecular organic layer. As the length of 4-nitrobenzene molecule is ≈ 0.8 nm, the film prepared by spontaneous modification on gold is consistent with a multilayer structure comprising from 2 to 3 monolayers [27]. After spontaneous modification of gold by ADT-C_8F_{17}, organic layer is close to a monolayer, (length of 4-(heptadecafluorooctyl)benzene molecule is ≈ 1.6 nm). Hence, we suppose that formation of monolayer structure can be explained by hindered attack of formed on surface 4-(heptadecafluorooctyl)phenyl layers, i.e. the effect that is typical for sterically

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hindered molecules [28]. Therefore, even electrochemical modification of gold by ADT-C_8F_{17} led to formation of thin multilayer (4 molecules). However, in the case of ADT-NO_2, we observed formation of structures with more than 8 monolayers of nitrobenzene (7.1±0.3 nm), what is consistent with previously published data [29].

Spatial distribution of elements on the samples surface after OFGs grafting was determined using SEM-EDS methods, on the 1x1 μm2 samples surface (Figure 2, left). Nitrogen and fluorine are specific markers for ADT-NO_2 and ADT-C_8F_{17} for the presented EDX maps of nitrogen (yellow) and fluorine (blue). In all cases the implementation of electro-induced modification mechanism led to significantly greater concentration of nitrogen and fluorine. The gold surface was covered homogeneously – the large amount of small dots.

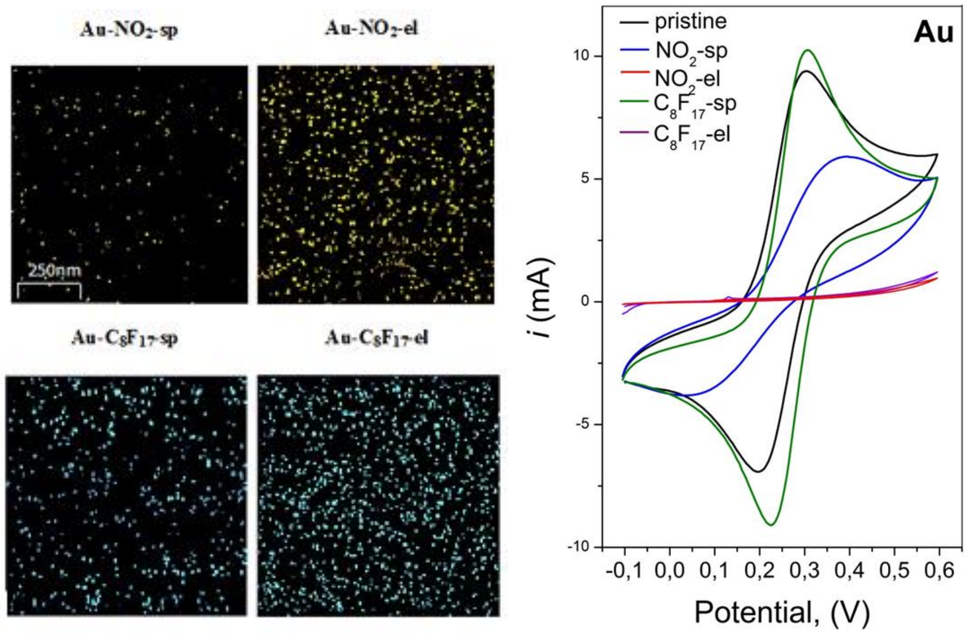

Figure 2. SEM-EDS mapping of nitrogen (yellow) and fluorine (blue) on gold and silver modified films (left). CVA curves measured on the Au thin films with covalently modified surface (right)

The surface blocking due to OFGs grafting was examined by CVA methods performed using the solution of hexacyanoferrate (II) for gold (Figure 2, right). On the CVA curves, measured on pristine gold films the apparent positive and negative peaks located at 0.33 V are attributed to the ferrate oxidation and reduction. After grafting of ADT-NO_2 by the spontaneous mechanism the peak becomes less pronounced, due to particular surface blocking by OFGs. When the electrochemically induced modification was applied, the ferrate-related peaks fully disappeared, indicating the full blocking of surface - the hexacyanoferrate (II) cannot reach the metal surface. The situation was similar in the case of ADT-C_8F_{17} grafted by electrochemical mechanism when the hexacyanoferrate (II) oxidation/reduction peak is also suppressed. However, spontaneous grafting of ADT-C_8F_{17} do not lead to full peak suppression, indicating the presence of the large number of unlocked seats, probably due to formation of close to monolayer structure of grafted OFGs.

It may be concluded that XPS, EDS, and CVA methods confirm grafting of ADTs to the thin metal films. After confirmation of modification process, the possibility to graft various “active” OFGs was studied (ADT-NH_2 and ADT-COOH). First of all the surface wettability (contact angle) was studied in dependence on the grafted OFGs and results are presented in the Figure 3.

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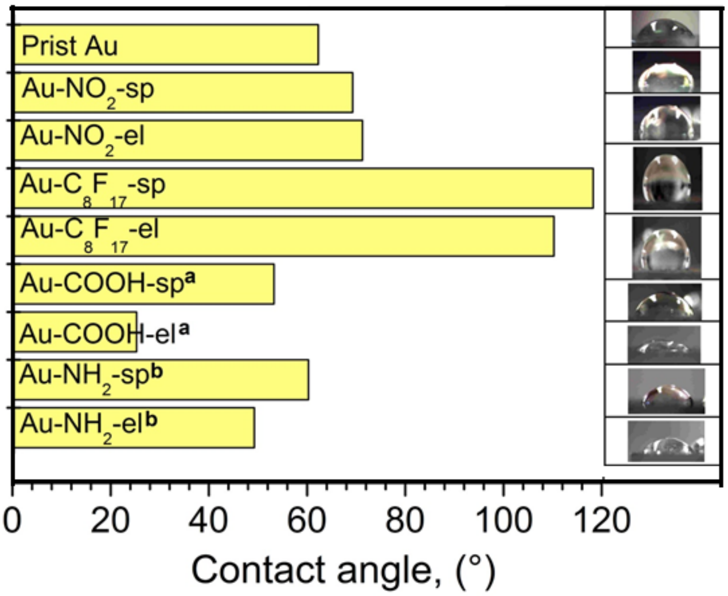

Figure 3. Surface wettability (contact angle and water drop) of pristine and modified Au film by ADTs. (a-contact angle after treatment by 1.0 % Na2CO3, b - contact angle after treatment by 0.5 % HCl).

As could be expected, the presence of carboxyl groups decreases the water contact angle, which on the other hand is increased by hydrophobic groups (nitro, amino). Treatment of amino and carboxyl groups by HCl and Na_2CO_3 results in expected decrease of contact angle due to salts formation. In the case of ADT-C_8F_{17} grafting unexpected results were obtained, the grafting significantly increased water contact angle, but the effect is more pronounced in the case of spontaneous grafting. This fact can be explained by orderliness of grafted aryl layers – “island-like” structure of spontaneously grafted ADT-C_8F_{17} may be an additional factors affecting the contact angle (similarly, higher surface roughness can reduce surface wettability).

Finally, the plasmonics properties of the metal surface were tested using the UV-Vis and Raman spectroscopy. Results of UV-Vis measurements are presented in the Figure 4, right. It is well known, that the position of plasmon resonance depends on the dielectric constant of medium surrounding metal nanostructures, namely electron density in the nanostructure and electron scattering function on the metal/dielectric boundary. In the case of gold layer (Figures), the plasmon resonance peak appeared in the near IR range, which is typical for cluster structure of sputtered gold layer. Modification of gold surface shifts the plasmon peak position to longer wavelength. The shift was more pronounced in the case of electrochemical modification because the larger part of plasmon evanescent wave is affected by the thicker organic film.

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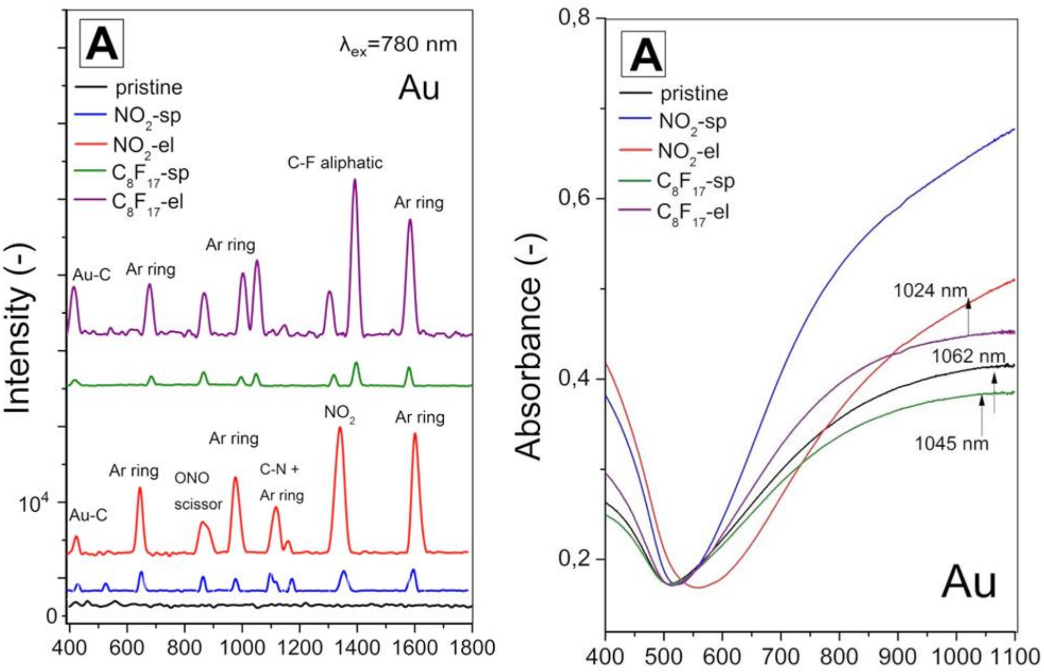

Figure 4. Raman spectra of ADTs covalently bounded to plasmon-active Au surfaces (left). UV-Vis spectra of pristine Au thin films measured before and after covalent modification by ADTs (right)

Typical proof of the plasmon activity is sufficient enhancement of OFGs Raman scattering, when they are closed to plasmon-active surface. Raman spectra were also collected in order to confirm the presence of corresponding OFGs on the surface of films (Figure 4, left). Taking into account of UV-Vis spectra of modified gold excitation wavelengths, close to plasmon absorption band, was chosen – 780 nm. Spectra of pristine gold films did not show any significant Raman bands. After spontaneous and electrically induced modification of gold and silver by OFGs expected Raman peaks occurred. The pronounced nature of the peaks in the Figure 8 indicates real enhancement of OFGs Raman scattering signal, due to significant energy focusing in the near-surface volume after photon-plasmon transition. The spectra of films after electrochemical treatment were significantly enhanced in comparison with spontaneous grafting due to the multilayer nature of OFGs layer. It should be also noted, that low intensity bands at approximately 400-440 cm-1 correspond with covalent bond Au-C, which were also observed at 433 cm-1. Their presence indicates the covalent binding of OFGs to metal surface.

4. Conclusion

Thin gold films of plasmon-active metal were grafted with various organic functional groups using ADTs spontaneous or electrochemically induced procedures. 4-nitrobenzediazonim tosylate and 4-(heptadecafluorooctyl) were used as model modification agent and modification by 4-aminobenzenediazonium tosylate and 4-carboxy benzenediazonium tosylate was performed to induce the specific changes of surface properties or create specific and selective sites for further modification. After grafting the surface and optical properties were characterized by the wide range of techniques. The possibility of changing the thickness of organic layer, modification of surface charge and wettability, particular of full surface blocking were demonstrated. Spontaneous reaction creates the short, approximately monomolecular films of organic compounds and could be used in the field of SPR or SERS sensors. Electrochemically induced activation gives the thicker layer of the organic compounds on the metal surface and it could find application in the field of tunable plasmonic devices or plasmon-based lasers.

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